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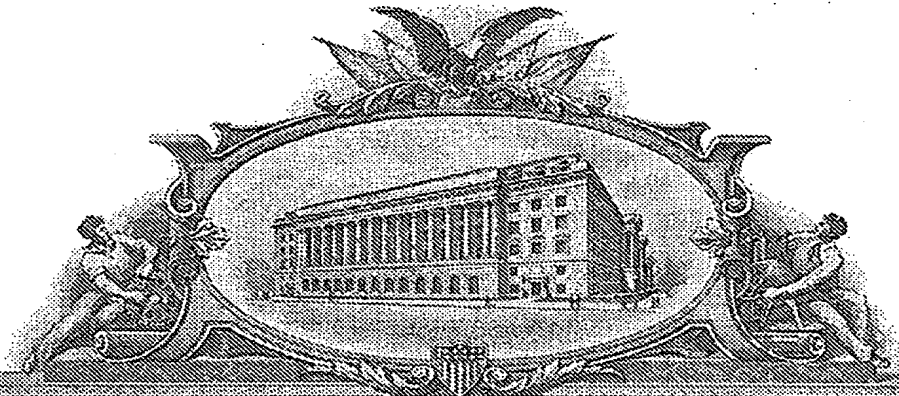
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**APPLICATION NUMBER: 60/534,112**

**FILING DATE: *January 05, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US05/00073***



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**PROVISIONAL APPLICATION**  
 Under Rule 53(c)

Sir:

Herewith is a **PROVISIONAL APPLICATION**  
 Title: **ATOM MODELS AND APPLICATIONS**

Our Order No. 50-0687	<b>62226-AM</b>	
	<b>C#</b>	<b>M#</b>
Atty. Dkt.	<b>62-226-ATOM-MODEL</b>	
	<b>M#</b>	<b>Client Ref</b>

including:

Date: January 5, 2004

1. Specification: 63 pages      2. ☐ Specification in non-English      3. ☐ Drawings:        sheet(s)

4. The invention ☐ was ☒ was not made by, or under a contract with, an agency of the U.S. Government.  
 If yes, Government agency/contact # = \_\_\_\_\_

5. ☐ Attached is an assignment and cover sheet. Please return the recorded assignment to the undersigned.

6. ☒ Applicant(s) claims "small entity" status under Rules 9 & 27.

7. ☐ Attached:

8. This application is made by the following named inventor(s) (Double check instructions for accuracy.):

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**APPLICATION UNDER UNITED STATES PATENT LAWS**

**Invention: ATOM MODELS AND APPLICATIONS**

**Inventor(s): Randell L. Mills**

**Attorney Docket No: 62226-AM**

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**THIS IS A PROVISIONAL PATENT APPLICATION**

**SPECIFICATION**

### THREE, FOUR, FIVE, SIX, SEVEN, EIGHT, NINE, AND TEN-ELECTRON ATOMS

#### THREE-ELECTRON ATOMS

As is the case for one and two-electron atoms shown in the corresponding sections, three through ten-electron atoms can also be solved exactly using the results of the solutions of the preceding atoms. For example, three-electron atoms can be solved exactly using the results of the solutions of the one and two-electron atoms.

#### THE LITHIUM ATOM

For  $Li^+$ , there are two spin-paired electrons in an orbitsphere with

$$r_1 = r_2 = a_0 \left[ \frac{1}{2} - \frac{\sqrt{3}}{6} \right] \quad (10.1)$$

as given by Eq. (7.19) where  $r_n$  is the radius of electron  $n$  which has velocity  $v_n$ . The next electron is added to a new orbitsphere because of the repulsive diamagnetic force between the two spin-paired electrons and the spin-unpaired electron. This repulsive diamagnetic force is due to the interaction of the magnetic field of the outer spin-unpaired electron on the electron current of the two spin-paired electrons of the inner shell. The diamagnetic force on the outer electron is determined by first considering the central force on each electron of the inner shell due to the magnetic flux  $B$  of the outer electron that follows from Purcell [1]

$$\mathbf{F} = \frac{2m_e v_n \Delta v}{r} \mathbf{i}_r \quad (10.2)$$

where  $\mathbf{i}_r$  is defined as the radial vector in the direction of the central electric field of the nucleus and

$$\frac{\Delta v}{r} = \frac{eB}{2m_e} \quad (10.3)$$

The velocity  $v_n$  is given by the boundary condition for no radiation as follows:

$$v_1 = \frac{\hbar}{m_e r_1} \quad (10.4)$$

where  $r_1$  is the radius of the first orbitsphere; therefore, the force on each of the inner electrons is given as follows:

$$\mathbf{F} = \frac{\hbar e B}{m_e r_1} \mathbf{i}_r \quad (10.5)$$

The change in magnetic moment,  $\Delta m$ , of each electron of the inner shell



due to the magnetic flux  $B$  of the outer electron is [1]

$$\Delta m = -\frac{e^2 r_1^2 B}{4 m_e} \quad (10.6)$$

The diamagnetic force on the outer electron due to the two inner shell electrons is in the opposite direction of the force given by Eq. (10.5), and this diamagnetic force on the outer electron is proportional to the sum of the changes in magnetic moments of the two inner electrons due to the magnetic flux  $B$  of the outer electron. The two electrons are spin-paired and the velocities are mirror opposites. Thus, the change in velocity of each electron treated individually (Eq. (10.3)) due to the magnetic flux  $B$  would be equal and opposite. However, the two paired electrons may be treated as one with twice the mass where  $m_e$  is replaced by  $2m_e$  in Eq. (10.6). In this case, the paired electrons spin together about the field axis to cause a reduction in the flux according to Lenz's law. It is then apparent that the force given by Eq. (10.5) is proportional to the flux  $B$  of the outer electron; whereas, the total of the change in magnetic moments of the inner shell electrons given by Eq. (10.6) applied to the combination of the inner electrons is proportional to one eighth of the flux,  $B$ . Thus, the force on the outer electron due to the reaction of the inner shell to the flux of the outer electron is given as follows:

$$F_{\text{diamagnetic}} = -\frac{\hbar}{8 r_1} \frac{e B}{m_e} \mathbf{i}_r \quad (10.7)$$

where  $r_1$  is the radial distance of the first orbitsphere from the nucleus. The magnetic flux,  $B$ , is supplied by the constant field inside the orbitsphere of the outer electron at radius  $r_3$  and is given by the product of  $\mu_o$  times Eq. (1.120).

$$B = \frac{\mu_o e \hbar}{m_e r_3^3} \quad (10.8)$$

The result of substitution of Eq. (10.8) into Eq. (10.7) is

$$F_{\text{diamagnetic}} = -\left[ \frac{e^2 \mu_o}{2 m_e r_3} \right] \frac{\hbar^2}{4 m_e r_1^2} \mathbf{i}_r \quad (10.9)$$

The term in brackets can be expressed in terms of the fine structure constant,  $\alpha$ . From Eqs. (1.144-1.148)

$$\frac{e^2 \mu_o}{2 m_e r_3} = 2 \pi \alpha \frac{v}{c} \quad (10.10)$$

It is demonstrated in the Two Electron Atom section that the relativistic correction to Eq. (10.9) is  $\frac{1}{Z}$  times the reciprocal of Eq. (10.10).  $Z$  for electron three is one; thus, one is substituted for the term in brackets in Eq. (10.9).

The force must be corrected for the vector projection of the velocity onto the z-axis. As given in the Spin Angular Momentum of the Orbitsphere with  $\ell=0$  section, the application of a z directed magnetic field of electron three given by Eq. (1.120) to the two inner orbitspheres gives rise to a diamagnetic field and a projection of the angular momentum of electron three onto an axis which precesses about the z-axis of  $\sqrt{\frac{3}{4}}\hbar$ . The projection of the force between electron three and electron one and two is equivalent to that of the angular momentum onto the axis which precesses about the z-axis, and is  $\sqrt{s(s+1)} = \sqrt{\frac{3}{4}}$  times that of a point mass. Thus, Eq. (10.9) becomes

$$F_{\text{diamagnetic}} = -\frac{\hbar^2}{4m_e r_3^2 r_1} \sqrt{s(s+1)} i_r \quad (10.11)$$

#### THE RADIUS OF THE OUTER ELECTRON OF THE LITHIUM ATOM

The radius for the outer electron is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic forces as follows:

$$\frac{m_e v_3^2}{r_3} = \frac{e^2}{4\pi\epsilon_0 r_3^2} - \frac{\hbar^2}{4m_e r_3^2 r_1} \sqrt{s(s+1)} \quad (10.12)$$

With  $v_3 = \frac{\hbar}{m_e r_3}$  (Eq. (1.56)),  $r_1 = a_0 \left[ \frac{1}{2} - \frac{\sqrt{3/4}}{6} \right]$  (Eq. (7.19)), and  $s = \frac{1}{2}$ , we solve for  $r_3$ .

$$r_3 = \frac{a_0}{\left[ 1 - \frac{\sqrt{3/4}}{4 \left( \frac{1}{2} - \frac{\sqrt{3/4}}{6} \right)} \right]} \quad (10.13)$$

$$r_3 = 2.5559 a_0$$

#### THE IONIZATION ENERGY OF LITHIUM

From Eq. (1.233), the magnitude of the energy stored in the electric field is

$$\frac{e^2}{8\pi\epsilon_0 r_3} = 5.318 \text{ eV} \quad (10.14)$$

The magnetic field of the outer electron changes the angular velocities



of the inner electrons. However, the magnetic field of the outer electron provides a central Lorentzian force which exactly balances the change in centrifugal force because of the change in angular velocity [1]. Thus, the electric energy of the inner orbitsphere is unchanged upon ionization. The magnetic field of the outer electron, however, also changes the magnetic moment,  $m$ , of each of the inner orbitsphere electrons. From Eq. (10.6), the change in magnetic moment,  $\Delta m$ , (per electron) is

$$\Delta m = -\frac{e^2 r_1^2}{4m_e} B \quad (10.15)$$

where  $B$  is the magnetic flux of the outer electron given by the product of  $\mu_o$  times Eq. (1.120).

$$B = \frac{\mu_o e \hbar}{m_e r_3^3} \quad (10.16)$$

Substitution of Eq. (10.16) and  $2m_e$  for  $m_e$  (because there are two electrons) into Eq. (10.15) gives

$$\Delta m = -\left[ \frac{e^2 \mu_o}{2m_e r_3} \right] \frac{e \hbar r_1^2}{4m_e r_3^2} \quad (10.17)$$

Furthermore, we know from Eqs. (10.9) and (10.11) that the term in brackets is replaced by  $\sqrt{s(s+1)}$ .

$$\Delta m = -\frac{e \hbar r_1^2}{4m_e r_3^2} \sqrt{s(s+1)} \quad (10.18)$$

Substitution of Eq. (10.1) for  $r_1$ , Eq. (10.13) for  $r_3$ , and given that the magnetic moment of an electron is one Bohr magneton according to Eq. (1.99),

$$\mu_B = \frac{e \hbar}{2m_e} \quad (10.19)$$

the fractional change in magnetic moment of an inner shell electron,  $\Delta m_f$ , is given as follows:

$$\Delta m_f = \frac{\frac{e \hbar r_1^2 \sqrt{s(s+1)}}{4m_e r_3^2}}{\frac{e \hbar}{2m_e}} \quad (10.20)$$

$$= \frac{1}{2} \frac{r_1^2}{r_3^2} \sqrt{s(s+1)} \quad (10.21)$$

With  $r_1$  given by Eq. (10.1),  $r_3$  given by Eq. (10.13), and  $s = \frac{1}{2}$ , the fractional change in magnetic moment of the two inner shell electrons is

$$\Delta m_f = \frac{\left[ a_0 \left[ \frac{1}{2} - \frac{\sqrt{3}}{6} \right] \right]^2 \sqrt{\frac{3}{4}}}{\left[ \frac{a_0}{1 - \frac{\sqrt{3}}{4}} \left( \frac{1}{2} - \frac{\sqrt{3}}{6} \right) \right]^2} \quad (10.22)$$

$$\Delta m_f = 0.01677$$

We add one (corresponding to  $m_f$ ) to  $\Delta m_f$  which is the fractional change in the magnetic moment. The energy stored in the magnetic field is proportional to the magnetic field strength squared as given by Eq. (1.122); thus, the sum is squared

$$(1.0168)^2 = 1.03382 \quad (10.23)$$

Thus, the change in magnetic energy of the inner orbitsphere is 3.382 %, so that the corresponding energy  $\Delta E_{mag}$  is

$$\Delta E_{mag} = 0.03382 \text{ eV} \times 2.543 \text{ eV} = 0.0860 \text{ eV} \quad (10.24)$$

where the magnetic energy of the inner electrons given in Table 7.1 is 2.543 eV. Then the ionization energy of the lithium atom is given by Eqs. (10.13-10.14) and (10.24):

$$E(\text{ionization}; \text{Li}) = \frac{(Z-2)e^2}{8\pi\epsilon_0 r_3} + \Delta E_{mag} \quad (10.25)$$

$$= 5.3178 \text{ eV} + 0.0860 \text{ eV} = 5.4038 \text{ eV}$$

The experimental ionization energy of lithium is 5.392 eV [2-3].

### THREE-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 3$

Three-electron atoms having  $Z > 3$  possess an electric field of

$$\mathbf{E} = \frac{(Z-3)e}{4\pi\epsilon_0 r^2} \mathbf{i}_r \quad (10.26)$$

for  $r > r_3$ . For three-electron atoms having  $Z > 3$ , the diamagnetic force given by Eq. (10.11) is unchanged. However, for three-electron atoms having  $Z > 3$ , an electric field exists for  $r > r_3$ . This electric field gives rise

to an additional diamagnetic force term which adds to Eq. (10.11). The additional diamagnetic force is derived as follows. The diamagnetic force repels the third (outer) electron, and the electric force attracts the third electron. Consider the reverse of ionization where the third electron is at infinity and the two spin paired electrons are at  $r_1 = r_2$  given by Eq. (7.19).

Power must be conserved as the net force of the diamagnetic and electric forces cause the third electron to move from infinity to its final radius. Power flow is given by the Poynting Power Theorem:

$$\nabla \cdot (\mathbf{E} \times \mathbf{H}) = -\frac{\delta}{\delta t} \left[ \frac{1}{2} \mu_o \mathbf{H} \cdot \mathbf{H} \right] - \frac{\delta}{\delta t} \left[ \frac{1}{2} \epsilon_o \mathbf{E} \cdot \mathbf{E} \right] - \mathbf{J} \cdot \mathbf{E} \quad (10.27)$$

During binding, the radius of electron three decreases. The electric force

$$\mathbf{F}_{ele} = \frac{(Z-2)e^2}{4\pi\epsilon_o r_3^2} \mathbf{i}_r \quad (10.28)$$

increases the stored electric energy which corresponds to the power term,  $-\frac{\delta}{\delta t} \left[ \frac{1}{2} \epsilon_o \mathbf{E} \cdot \mathbf{E} \right]$ , of Eq. (10.27). The diamagnetic force given by Eq. (10.7) changes the stored magnetic energy which corresponds to the power term,  $-\frac{\delta}{\delta t} \left[ \frac{1}{2} \mu_o \mathbf{H} \cdot \mathbf{H} \right]$ , of Eq. (10.27). An additional diamagnetic force arises when  $Z-3 > 0$ . This diamagnetic force corresponds to that given by Purcell [1] for a charge moving in a central field having an imposed magnetic field perpendicular to the plane of motion. The second diamagnetic force  $\mathbf{F}_{diamagnetic2}$  is given by

$$\mathbf{F}_{diamagnetic2} = -2 \frac{m_e \Delta v^2}{r_1} \mathbf{i}_r \quad (10.29)$$

where  $\Delta v$  is derived from Eq. (10.3). The result of substitution of  $\Delta v$  into Eq. (10.29) is

$$\mathbf{F}_{diamagnetic2} = -\frac{2m_e}{r_1} \left[ \frac{er_1 B}{2m_e} \right]^2 \mathbf{i}_r \quad (10.30)$$

The magnetic flux,  $B$ , at electron three for  $r < r_3$  is given by the product of  $\mu_o$  times Eq. (1.120). The result of the substitution of the flux into Eq. (10.30) is

$$\mathbf{F}_{diamagnetic2} = -2 \left[ \frac{e^2 \mu_o}{2m_e r_3} \right]^2 \frac{r_1 \hbar^2}{m_e r_3^4} \mathbf{i}_r \quad (10.31)$$

The term in brackets can be expressed in terms of the fine structure constant,  $\alpha$ . From Eqs. (1.144-1.148)

$$\frac{Z_1 e^2 \mu_o}{2m_e r_3} = 2\pi\alpha Z_1 \frac{v}{c} \quad (10.32)$$

It is demonstrated in the Two Electron Atom section that the relativistic correction to Eq. (10.31) is  $\frac{1}{Z}$  times the reciprocal of Eq. (10.32). Consider the case wherein  $Z_1$  of Eq. (10.32) is different from  $Z = Z_2$  of Eq. (7.13) in order to maintain relativistic invariance of the electron angular momentum and magnetic moment. The relativistic correction to Eq. (10.31) can be considered the product of two corrections—a correction of electron three relative to electron one and two and electron one and two relative to electron three. In the former case,  $Z_1$  and  $Z_2 = 1$  which corresponds to electron three. In the latter case,  $Z_1 = Z - 3$ , and  $Z_2 = Z - 2$  which corresponds to  $r_3^+$ , infinitesimally greater than the radius of the outer orbitsphere and  $r_3^-$ , infinitesimally less than the radius of the outer orbitsphere, respectively, where  $Z$  is the nuclear charge. Thus,  $\frac{Z-3}{Z-2}$  is substituted for the term in brackets in Eq. (10.31). The force must be corrected for the vector projection of the velocity onto the z-axis. As given in the Spin Angular Momentum of the Orbitsphere with  $\ell = 0$  section, the application of a z directed magnetic field of electron three given by Eq. (1.120) to the two inner orbitspheres gives rise to a diamagnetic field and a projection of the angular momentum of electron three onto an axis which precesses about the z-axis of  $\sqrt{\frac{3}{4}}\hbar$ . The projection of the force between electron three and electron one and two is equivalent to that of the angular momentum onto the axis which precesses about the z-axis, and is  $\sqrt{s(s+1)} = \sqrt{\frac{3}{4}}$  times that of a point mass. Thus, Eq. (10.31) becomes

$$F_{\text{diamagnetic2}} = -2 \frac{(Z-3)r_1\hbar^2}{(Z-2)m_e r_3^4} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.33)$$

As given previously in the Two Electron section, this force corresponds to the dissipation term of Eq. (10.27),  $\mathbf{J} \cdot \mathbf{E}$ . The current  $\mathbf{J}$  is proportional to the sum of one for the outer electron and two times two—the number of spin paired electrons. For the inner electrons, the factor of two arises because they possess mutual inductance which doubles their contribution to  $\mathbf{J}$ . (Recall the general relationship that the current is equal to the flux divided by the inductance.) Thus, the second diamagnetic force is

$$F_{\text{diamagnetic2}} = -2 \left[ \frac{Z-3}{Z-2} \right] \frac{(1+4)r_1\hbar^2}{m_e r_3^4} \sqrt{s(s+1)} \mathbf{i}_r; \quad s = \frac{1}{2} \quad (10.34)$$

$$F_{\text{diamagnetic2}} = - \left[ \frac{Z-3}{Z-2} \right] \frac{r_1\hbar^2}{m_e r_3^4} 10\sqrt{3/4} \mathbf{i}_r \quad (10.35)$$

### THE RADIUS OF THE OUTER ELECTRON OF THREE-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 3$

The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic forces as follows:

$$\frac{m_e v_3^2}{r_3} = \frac{(Z-2)e^2}{4\pi\epsilon_0 r_3^2} - \frac{\hbar^2}{4m_e r_3^2 r_1} \sqrt{s(s+1)} - \left[ \frac{Z-3}{Z-2} \right] \frac{r_1 \hbar^2}{r_3^4 m_e} 10\sqrt{s(s+1)} \quad (10.36)$$

With  $v_3 = \frac{\hbar}{m_e r_3}$  (Eq. (1.56)),  $r_1 = a_0 \left( \frac{1}{Z-1} - \frac{\sqrt{s(s+1)}}{Z(Z-1)} \right)$  (Eq. (7.19)), and  $s = \frac{1}{2}$ , we solve for  $r_3$  using the quadratic formula or reiteratively.

$$r_3 = \frac{1 + \left[ \frac{Z-3}{Z-2} \right] \frac{r_1}{r_3} 10\sqrt{\frac{3}{4}}}{\left[ \frac{(Z-2)}{a_0} - \frac{\sqrt{\frac{3}{4}}}{4r_1} \right]} \quad (10.37)$$

The quadratic equation corresponding to Eq. (10.37) is

$$r_3^2 - \frac{r_3}{\left[ \frac{(Z-2)}{a_0} - \frac{\sqrt{\frac{3}{4}}}{4r_1} \right]} - \frac{\left[ \frac{Z-3}{Z-2} \right] r_1 10\sqrt{\frac{3}{4}}}{\left[ \frac{(Z-2)}{a_0} - \frac{\sqrt{\frac{3}{4}}}{4r_1} \right]} = 0 \quad (10.38)$$

The solution of Eq. (10.38) using the quadratic formula is

$$r_3 = \frac{\frac{a_0}{\left[ (Z-2) - \frac{\sqrt{\frac{3}{4}}}{4r_1} \right]} \pm a_0 \sqrt{\frac{1}{\left[ (Z-2) - \frac{\sqrt{\frac{3}{4}}}{4r_1} \right]^2} + 4 \frac{\left[ \frac{Z-3}{Z-2} \right] r_1 10\sqrt{\frac{3}{4}}}{\left[ (Z-2) - \frac{\sqrt{\frac{3}{4}}}{4r_1} \right]}}}{2}, \quad r_1 \text{ in units of } a_0 \quad (10.39)$$

$$r_3 = \frac{\left[ \frac{a_o}{(Z-2) - \frac{\sqrt{3/4}}{4r_1}} \right] \left[ 1 \pm \sqrt{1 + 4 \left[ \frac{Z-3}{Z-2} \right] r_1 10 \sqrt{\frac{3}{4}} \left[ (Z-2) - \frac{\sqrt{3/4}}{4r_1} \right]} \right]}{2}, \quad r_1 \text{ in units of } a_o \quad (10.40)$$

$$r_3 = \frac{\left[ \frac{a_o}{(Z-2) - \frac{\sqrt{3/4}}{4r_1}} \right] \left[ 1 \pm \sqrt{1 + 4(Z-3)r_1 10 \sqrt{\frac{3}{4}} - \left[ \frac{Z-3}{Z-2} \right] \frac{30}{4}} \right]}{2}, \quad r_1 \text{ in units of } a_o \quad (10.41)$$

$$r_3 = \frac{\left[ \frac{a_o}{(Z-2) - \frac{\sqrt{3/4}}{4 \left( \frac{1}{Z-1} - \frac{\sqrt{3/4}}{Z(Z-1)} \right)}} \right] \left[ 1 \pm \sqrt{1 + 4(Z-3) \left( \frac{1}{Z-1} - \frac{\sqrt{3/4}}{Z(Z-1)} \right) 10 \sqrt{\frac{3}{4}} - \left[ \frac{Z-3}{Z-2} \right] \frac{30}{4}} \right]}{2} \quad (10.42)$$

The positive root of Eq. (10.42) must be taken in order that  $r_3 > 0$ .

### THE IONIZATION ENERGIES OF THREE-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 3$

The energy stored in the electric field,  $E(\text{electric})$ , is

$$E(\text{electric}) = -\frac{(Z-2)e^2}{8\pi\epsilon_0 r_3} \quad (10.43)$$

where  $r_3$  is given by Eq. (10.42). The magnetic field of the outer electron changes the velocities of the inner electrons. However, the magnetic field of the outer electron provides a central Lorentzian field which balances the change in centrifugal force because of the change in velocity. Thus, the electric energy of the inner orbitsphere is unchanged upon ionization. The change in the velocities of the inner electrons upon ionization gives rise to a change in kinetic energies of the inner electrons. The change in velocity,  $\Delta v$ , is given by Eq. (10.3)

$$\Delta v = \frac{er_1 B}{2m_e} \quad (10.44)$$

Substitution of the flux,  $B$ , given by the product of  $\mu_o$  and Eq. (1.120),

into Eq. (10.43) is

$$\Delta v = \left[ \frac{e^2 \mu_o}{2 m_e r_1} \right] \frac{r_1^2 \hbar}{m_e r_3^3} \quad (10.45)$$

It is demonstrated in the One Electron Atom section and the Two Electron Atom section (at Eq. (7.14)) that the relativistic correction to Eq. (10.45) is  $\frac{1}{Z}$  times the reciprocal of the term in brackets. In this case,  $Z$  corresponding to electron three is one; thus, one is substituted for the term in brackets in Eq. (10.45). Thus, Eq. (10.45) becomes,

$$\Delta v = \frac{r_1^2 \hbar}{r_3^3 m_e} \quad (10.46)$$

where  $r_1$  is given by Eq. (7.19), and  $r_3$  is given by Eq. (10.42). The change in kinetic energy,  $\Delta E_T$ , of the two inner shell electrons is given by

$$\Delta E_T = 2 \frac{1}{2} m_e \Delta v^2 \quad (10.47)$$

The ionization energy is the sum of the electric energy, Eq. (10.43), and the change in the kinetic energy, Eq. (10.47), of the inner electrons.

$$E(\text{Ionization}) = E(\text{Electric}) + E_T \quad (10.48)$$

The relativistic correction to Eq. (10.48) is given by 1.) relativistically correcting the radius of the inner paired electrons  $r_1$ , 2.) using the relativistically corrected  $r_1$  to determine  $r_3$ , which is then relativistically corrected. The relativistically corrected  $r_1$  is given by dividing the radius given Eq. (7.19) by  $\gamma^*$  of Eq. (1.250)

$$r_2 = r_1 = \frac{r_1}{\gamma} = \frac{a_0 \left( \frac{1}{Z-1} - \frac{\sqrt{s(s+1)}}{Z(Z-1)} \right)}{2\pi \sqrt{1 - \left( \frac{v}{c} \right)^2} \sin \left[ \frac{\pi}{2} \left( 1 - \left( \frac{v}{c} \right)^2 \right)^{3/2} \right] + \cos \left[ \frac{\pi}{2} \left( 1 - \left( \frac{v}{c} \right)^2 \right)^{3/2} \right]}, \quad s = \frac{1}{2} \quad (10.49)$$

where the velocity is given by Eq. (1.56) with the radius given by Eq. (7.19). Similarly, the relativistically corrected  $r_3$  is given by dividing the radius given Eq. (10.41) by  $\gamma^*$  of Eq. (1.250)

$$r_3 = \frac{r_3'}{\gamma} = \frac{\frac{a_0}{\left[ (Z-2) - \frac{\sqrt{3}}{4} \right]} \left[ 1 + \sqrt{1 + 4(Z-3)r_1 10 \sqrt{\frac{3}{4} - \left[ \frac{Z-3}{Z-2} \right] \frac{30}{4}}} \right]}{2\pi \sqrt{1 - \left( \frac{v}{c} \right)^2} \sin \left[ \frac{\pi}{2} \left( 1 - \left( \frac{v}{c} \right)^2 \right)^{3/2} \right] + \cos \left[ \frac{\pi}{2} \left( 1 - \left( \frac{v}{c} \right)^2 \right)^{3/2} \right]}, \quad r_1 \text{ in units of } a_0 \quad (10.50)$$

where  $r_1$  is given by Eq. (10.49) and the velocity is given by (1.56) with the radius given by Eq. (10.42). The ionization energies are given by Eq. (10.48) wherein the relativistically corrected radii given by Eqs. (10.49-10.50) are used in the sum of the electric energy, Eq. (10.43), and the change in the kinetic energy, Eq. (10.47), of the inner electrons. The ionization energies for several three-electron atoms are given in Table 10.1.



Table 10.1. Ionization energies for some three-electron atoms.

3 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_3$ ( $a_0$ ) <sup>b</sup>	Electric Energy <sup>c</sup> (eV)	$\Delta v$ <sup>d</sup> (m/s)	$\Delta E_T$ <sup>e</sup> (eV)	Theoretical Ionization Energies <sup>f</sup> (eV)	Experimental Ionization Energies <sup>g</sup> (eV)	Relative Error
<i>Li</i>	3	0.35566	2.55606	5.3230	1.6571E+04	1.5613E-03	5.40381	5.39172	-0.00224
<i>Be</i> <sup>+</sup>	4	0.26116	1.49849	18.1594	4.4346E+04	1.1181E-02	18.1706	18.21116	0.00223
<i>B</i> <sup>2+</sup>	5	0.20670	1.07873	37.8383	7.4460E+04	3.1523E-02	37.8701	37.93064	0.00160
<i>C</i> <sup>3+</sup>	6	0.17113	0.84603	64.3278	1.0580E+05	6.3646E-02	64.3921	64.4939	0.00158
<i>N</i> <sup>4+</sup>	7	0.14605	0.69697	97.6067	1.3782E+05	1.0800E-01	97.7160	97.8902	0.00178
<i>O</i> <sup>5+</sup>	8	0.12739	0.59299	137.6655	1.7026E+05	1.6483E-01	137.8330	138.1197	0.00208
<i>F</i> <sup>6+</sup>	9	0.11297	0.51621	184.5001	2.0298E+05	2.3425E-01	184.7390	185.186	0.00241
<i>Ne</i> <sup>7+</sup>	10	0.10149	0.45713	238.1085	2.3589E+05	3.1636E-01	238.4325	239.0989	0.00279
<i>Na</i> <sup>8+</sup>	11	0.09213	0.41024	298.4906	2.6894E+05	4.1123E-01	298.9137	299.864	0.00317
<i>Mg</i> <sup>9+</sup>	12	0.08435	0.37210	365.6469	3.0210E+05	5.1890E-01	366.1836	367.5	0.00358
<i>Al</i> <sup>10+</sup>	13	0.07778	0.34047	439.5790	3.3535E+05	6.3942E-01	440.2439	442	0.00397
<i>Si</i> <sup>11+</sup>	14	0.07216	0.31381	520.2888	3.6868E+05	7.7284E-01	521.0973	523.42	0.00444
<i>P</i> <sup>12+</sup>	15	0.06730	0.29102	607.7792	4.0208E+05	9.1919E-01	608.7469	611.74	0.00489
<i>S</i> <sup>13+</sup>	16	0.06306	0.27132	702.0535	4.3554E+05	1.0785E+00	703.1966	707.01	0.00539
<i>Cl</i> <sup>14+</sup>	17	0.05932	0.25412	803.1158	4.6905E+05	1.2509E+00	804.4511	809.4	0.00611
<i>Ar</i> <sup>15+</sup>	18	0.05599	0.23897	910.9708	5.0262E+05	1.4364E+00	912.5157	918.03	0.00601
<i>K</i> <sup>16+</sup>	19	0.05302	0.22552	1025.6241	5.3625E+05	1.6350E+00	1027.3967	1033.4	0.00581
<i>Ca</i> <sup>17+</sup>	20	0.05035	0.21350	1147.0819	5.6993E+05	1.8468E+00	1149.1010	1157.8	0.00751
<i>Sc</i> <sup>18+</sup>	21	0.04794	0.20270	1275.3516	6.0367E+05	2.0720E+00	1277.6367	1287.97	0.00802
<i>Ti</i> <sup>19+</sup>	22	0.04574	0.19293	1410.4414	6.3748E+05	2.3106E+00	1413.0129	1425.4	0.00869
<i>V</i> <sup>20+</sup>	23	0.04374	0.18406	1552.3606	6.7135E+05	2.5626E+00	1555.2398	1569.6	0.00915
<i>Cr</i> <sup>21+</sup>	24	0.04191	0.17596	1701.1197	7.0530E+05	2.8283E+00	1704.3288	1721.4	0.00992
<i>Mn</i> <sup>22+</sup>	25	0.04022	0.16854	1856.7301	7.3932E+05	3.1077E+00	1860.2926	1879.9	0.01043
<i>Fe</i> <sup>23+</sup>	26	0.03867	0.16172	2019.2050	7.7342E+05	3.4011E+00	2023.1451	2023	-0.00007
<i>Co</i> <sup>24+</sup>	27	0.03723	0.15542	2188.5585	8.0762E+05	3.7084E+00	2192.9020	2219	0.01176
<i>Ni</i> <sup>25+</sup>	28	0.03589	0.14959	2364.8065	8.4191E+05	4.0300E+00	2369.5803	2399.2	0.01235
<i>Cu</i> <sup>26+</sup>	29	0.03465	0.14418	2547.9664	8.7630E+05	4.3661E+00	2553.1987	2587.5	0.01326

<sup>a</sup> Radius of the paired inner electrons of three-electron atoms from Eq. (10.49).<sup>b</sup> Radius of the unpaired outer electron of three-electron atoms from Eq. (10.50).<sup>c</sup> Electric energy of the outer electron of three-electron atoms from Eq. (10.43).<sup>d</sup> Change in the velocity of the paired inner electrons due to the unpaired outer electron of three-electron atoms from Eq. (10.46).<sup>e</sup> Change in the kinetic energy of the paired inner electrons due to the unpaired outer electron of three-electron atoms from Eq. (10.47).<sup>f</sup> Calculated ionization energies of three-electron atoms from Eq. (10.48) for  $Z > 3$  and Eq. (10.25) for *Li*.<sup>g</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.1 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The lithium atom isoelectronic series is given in Table 10.1 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Li isoelectronic and Rydberg series, as well as direct experimental data.

#### FOUR-ELECTRON ATOMS

Four-electron atoms can be solved exactly using the results of the solutions of one, two, and three-electron atoms.

#### RADII OF THE OUTER ELECTRONS OF FOUR-ELECTRON ATOMS

For each three-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19):

$$r_1 = r_2 = a_0 \left[ \frac{1}{Z-1} - \frac{\sqrt{3}}{Z(Z-1)} \right] \quad (10.51)$$

and an unpaired electron with a radius  $r_3$  given by Eq. (10.42). For  $Z \geq 4$ , the next electron which binds to form the corresponding four-electron atom becomes spin-paired with the outer electron such that they become indistinguishable with the same radius  $r_3 = r_4$ . The corresponding spin-pairing force  $F_{mag}$  is given by Eq. (7.15):

$$F_{mag} = \frac{1}{Z} \frac{\hbar^2}{m_e r_4^3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.52)$$

The central forces given by Eq. (10.36) and Eq. (10.52) act on the outer electron to cause it to bind wherein the electric force on the outer-most electron due to the nucleus and the inner three electrons is given by Eq. (10.28) with the appropriate charge and radius:

$$F_{ele} = \frac{(Z-3)e^2}{4\pi\epsilon_0 r_4^2} \mathbf{i}_r \quad (10.53)$$

for  $r > r_3$ .

In addition to the paramagnetic spin-pairing force between the third electron initially at radius  $r_3$ , the pairing causes the diamagnetic interaction between the outer electrons and the inner electrons given by Eq. (10.11) to vanish, except for an electrodynamic effect for  $Z > 4$  described in the Two-Electron Atoms section, since upon pairing the magnetic field of the outer electrons becomes zero. Therefore, the force  $F_{mag2}$  is in the same direction as the spin-pairing force and is given by substitution of Eq. (7.4) with the radius  $r_4$  into Eq. (10.5):

$$F_{mag2} = \frac{\hbar e B}{2m_e r_1} = \frac{\mu_0 e^2 \hbar^2}{2m_e^2 r_1^3} \hat{i}_r \quad (10.54)$$

Then, from Eqs. (10.54) and (7.6-7.15), the diamagnetic force is given by

$$F_{mag2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_1^2} \sqrt{s(s+1)} \hat{i}_r \quad (10.55)$$

The outward centrifugal force on electron 4 is balanced by the electric force and the magnetic forces (on electron 4). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.52)), diamagnetic (Eqs. (10.11), (10.35), and (10.54)), and paramagnetic (Eq. (10.53)) forces as follows:

$$\frac{m_e v_4^2}{r_4} = \frac{(Z-3)e^2}{4\pi\epsilon_0 r_4^2} - \frac{\hbar^2}{4m_e r_4^2 r_1} \sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_4^2 r_1} \sqrt{s(s+1)} - \left[ \frac{Z-3}{Z-2} \right] \frac{r_1 \hbar^2}{r_4^4 m_e} 10 \sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_4^3} \sqrt{s(s+1)} \quad (10.56)$$

Substitution of  $v_4 = \frac{\hbar}{m_e r_4}$  (Eq. (1.56) and  $s = \frac{1}{2}$  into Eq. (10.56) gives:

$$\frac{\hbar^2}{m_e r_4^3} = \frac{(Z-3)e^2}{4\pi\epsilon_0 r_4^2} - \frac{\hbar^2}{4m_e r_4^2 r_1} \sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_4^2 r_1} \sqrt{\frac{3}{4}} - \left[ \frac{Z-3}{Z-2} \right] \frac{r_1 \hbar^2}{r_4^4 m_e} 10 \sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_4^3} \sqrt{\frac{3}{4}} \quad (10.57)$$

$$\left( \frac{(Z-3)e^2}{4\pi\epsilon_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\hbar^2}{m_e r_1} \sqrt{\frac{3}{4}} \right) \frac{1}{r_4^2} - \left[ \frac{Z-3}{Z-2} \right] \frac{r_1 \hbar^2}{r_4^4 m_e} 10 \sqrt{\frac{3}{4}} - \frac{\hbar^2}{m_e r_4^3} \left( 1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right) = 0 \quad (10.58)$$

The quadratic equation corresponding to Eq. (10.58) is

$$\left( \frac{(Z-3)e^2}{4\pi\epsilon_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\hbar^2}{m_e r_1} \sqrt{\frac{3}{4}} \right) r_4^2 - \frac{\hbar^2}{m_e} \left( 1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right) r_4 - \left[ \frac{Z-3}{Z-2} \right] \frac{r_1 \hbar^2}{m_e} 10 \sqrt{\frac{3}{4}} = 0 \quad (10.59)$$

$$r_4^2 - \frac{\frac{\hbar^2}{m_e} \left( 1 - \frac{\sqrt{3}}{4} \right)}{\left( \frac{(Z-3)e^2}{4\pi\epsilon_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\hbar^2}{m_e r_1} \sqrt{\frac{3}{4}} \right)} r_4 - \frac{\left[ \frac{Z-3}{Z-2} \right] \frac{r_1 \hbar^2}{m_e} 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-3)e^2}{4\pi\epsilon_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\hbar^2}{m_e r_1} \sqrt{\frac{3}{4}} \right)} = 0 \quad (10.60)$$

$$r_4^2 - \frac{\left( 1 - \frac{\sqrt{3}}{4} \right)}{\left( \frac{(Z-3)}{a_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{3}}{r_1} \right)} r_4 - \frac{\left[ \frac{Z-3}{Z-2} \right] r_1 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-3)}{a_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{3}}{r_1} \right)} = 0 \quad (10.61)$$

The solution of Eq. (10.61) using the quadratic formula is:

$$r_4 = r_3 = \frac{a_0 \left( 1 - \frac{\sqrt{3}}{4} \right) \pm a_0 \sqrt{\left( \left( 1 - \frac{\sqrt{3}}{4} \right)^2 + 4 \left[ \frac{Z-3}{Z-2} \right] r_1 10 \sqrt{\frac{3}{4}} \left( \frac{(Z-3)}{a_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{3}}{r_1} \right) \right)}}{2 \left( \frac{(Z-3)}{a_0} - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{3}}{r_1} \right)} \quad (10.62)$$

$r_1$  in units of  $a_0$

where  $r_1$  is given by Eq. (10.51) and also Eq. (7.19). The positive root of Eq. (10.62) must be taken in order that  $r_4 > 0$ . The final radius of electron 4,  $r_4$ , is given by Eq. (10.62); this is also the final radius of electron 3. The radii of several four-electron atoms are given in Table 10.2.

#### ENERGIES OF THE BERYLLIUM ATOM

The energy stored in the electric field,  $E(\text{electric})$ , is given by Eq. (10.43) with the appropriate charge and radius:

$$E(\text{electric}) = -\frac{(Z-3)e^2}{8\pi\epsilon_0 r_4} \quad (10.63)$$

The ionization energy is given by the sum of the electric energy and the diamagnetic and paramagnetic energy terms. The magnetic energy,  $E(\text{magnetic})$ , for an electron corresponding to a radius  $r_n$  given by Eq.

(7.30) is

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_n^3} \quad (10.64)$$

Since there is no source of dissipative power,  $\mathbf{J} \cdot \mathbf{E}$  of Eq. (10.27), to compensate for any potential change in the magnetic moments,  $\Delta m$ , of the inner electrons due to the ionization of an outer electron of the beryllium atom, there is a diamagnetic energy term in the ionization energy for this atom that follows from the corresponding term for the lithium atom. This term is given by Eqs. (10.15-10.24) wherein  $r_1$  is given by Eq. (10.51) with  $Z=4$  and  $r_3=r_4$  is given by Eq. (10.62). Thus, the change in magnetic energy of the inner orbitsphere is 5.144 %, so that the corresponding energy  $\Delta E_{\text{mag}}$  is

$$\Delta E_{\text{mag}} = 0.05144 \text{ eV} \times 6.42291 \text{ eV} = 0.33040 \text{ eV} \quad (10.65)$$

where the magnetic energy of the inner electrons is 6.42291 eV. In addition, there is a paramagnetic energy term  $E(\text{magnetic})$  corresponding to the ionization of a spin-paired electron from a neutral atom with a closed s-shell. The energy follows from that given for helium by Eqs. (7.28) and (7.30) wherein the electron radius for helium is replaced by the radius  $r_4$  of Eq. (10.62). Then, the ionization energy of the beryllium atom is given by Eqs. (7.28), (7.30), (10.25), and (10.62-10.65):

$$E(\text{ionization}; \text{Be}) = \frac{(Z-3)e^2}{8\pi\epsilon_0 r_4} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_4^3} + \Delta E_{\text{mag}} \quad (10.66)$$

$$= 8.9216 \text{ eV} + 0.03226 \text{ eV} + 0.33040 \text{ eV} = 9.28430 \text{ eV}$$

The experimental ionization energy of beryllium is 9.32263 eV [3].

#### THE IONIZATION ENERGIES OF FOUR-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 4$

The ionization energies for the four-electron atoms with  $Z > 4$  are given by the sum of the electric energy,  $E(\text{electric})$ , given by Eq. (10.63) and the magnetic energies. The paramagnetic energy term corresponding to the ionization of a spin-paired electron from an atom with an external electric field is given by Eqs. (7.30) and (7.47) wherein the electron radius for helium is replaced by the radius  $r_4$  of Eq. (10.62):

$$\text{Ionization Energy} = -\text{Electric Energy} - \frac{1}{Z} \text{Magnetic Energy} \quad (10.67)$$

Once the outer electrons of four-electron atoms with  $Z > 4$  become spin unpaired during ionization, the corresponding magnetic field changes the velocities of the inner electrons in the same manner as shown for the case of the outer electron of three-electron atoms with  $Z > 3$ . The magnetic effect is calculated for the remaining electron 3 at the radius  $r_4$  corresponding to condition of the derivation of Eq. (10.67)

that follows from Eqs. (7.30) and (7.47). Thus, change in velocity,  $\Delta v$ , in the four-electron-atom case is that of three-electron atoms given by Eq. (10.46) wherein the electron radius  $r_3$  is replaced by the radius  $r_4$  of Eq. (10.62).

Since the velocities of electrons one and two decrease during ionization in the case of four-electron atoms rather than increase as in the case of three-electron atoms, the corresponding kinetic energy decreases and the kinetic energy term given by Eq. (10.47) is the opposite sign in Eq. (10.48). Thus, the ionization energies of four-electron atoms with  $Z > 4$  given by Eqs. (10.48) and (10.67) with the electric energy (Eq. (10.63)), the magnetic energy (Eq. (10.64)), and the change in the kinetic energy of the inner electrons (Eq. (10.47)) are

$$E(\text{Ionization}) = -\text{Electric Energy} - \frac{1}{Z} \text{Magnetic Energy} - E_r \quad (10.68)$$

The ionization energies for several four-electron atoms are given in Table 10.2. Since the radii,  $r_4$ , are greater than 10% of  $a_0$  corresponding to a velocity of less than  $1.5 \times 10^7$  m/s, the relativistic corrections are negligible and are not included in Table 10.2.

Table 10.2. Ionization energies for some four-electron atoms.

4 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_3$ ( $a_0$ ) <sup>b</sup>	Electric Energy <sup>c</sup> (eV)	Magnetic Energy <sup>d</sup> (eV)	$\Delta v$ <sup>e</sup> (m/s X $10^{-3}$ )	$\Delta E_T$ <sup>f</sup> (eV)	Theoretical Ionization Energies <sup>g</sup> (eV)	Experimental Ionization Energies <sup>h</sup> (eV)	Relative Error
Be	4	0.26116	1.52503	8.9178	0.03226	0.4207	0.0101	9.28430	9.32263	0.0041
B <sup>+</sup>	5	0.20670	1.07930	25.2016	0.0910	0.7434	0.0314	25.1627	25.15484	-0.0003
C <sup>2+</sup>	6	0.17113	0.84317	48.3886	0.1909	1.0688	0.0650	48.3125	47.8878	-0.0089
N <sup>3+</sup>	7	0.14605	0.69385	78.4029	0.3425	1.3969	0.1109	78.2765	77.4735	-0.0104
O <sup>4+</sup>	8	0.12739	0.59020	115.2148	0.5565	1.7269	0.1696	115.0249	113.899	-0.0099
F <sup>5+</sup>	9	0.11297	0.51382	158.8102	0.8434	2.0582	0.2409	158.5434	157.1651	-0.0088
Ne <sup>6+</sup>	10	0.10149	0.45511	209.1813	1.2138	2.3904	0.3249	208.8243	207.2759	-0.0075
Na <sup>7+</sup>	11	0.09213	0.40853	266.3233	1.6781	2.7233	0.4217	265.8628	264.25	-0.0061
Mg <sup>8+</sup>	12	0.08435	0.37065	330.2335	2.2469	3.0567	0.5312	329.6559	328.06	-0.0049
Al <sup>9+</sup>	13	0.07778	0.33923	400.9097	2.9309	3.3905	0.6536	400.2017	398.75	-0.0036
Si <sup>10+</sup>	14	0.07216	0.31274	478.3507	3.7404	3.7246	0.7888	477.4989	476.36	-0.0024
P <sup>11+</sup>	15	0.06730	0.29010	562.5555	4.6861	4.0589	0.9367	561.5464	560.8	-0.0013
S <sup>12+</sup>	16	0.06306	0.27053	653.5233	5.7784	4.3935	1.0975	652.3436	652.2	-0.0002
Cl <sup>13+</sup>	17	0.05932	0.25344	751.2537	7.0280	4.7281	1.2710	749.8899	749.76	-0.0002
Ar <sup>14+</sup>	18	0.05599	0.23839	855.7463	8.4454	5.0630	1.4574	854.1849	854.77	0.0007
K <sup>15+</sup>	19	0.05302	0.22503	967.0007	10.0410	5.3979	1.6566	965.2283	968	0.0029
Ca <sup>16+</sup>	20	0.05035	0.21308	1085.0167	11.8255	5.7329	1.8687	1083.0198	1087	0.0037
Sc <sup>17+</sup>	21	0.04794	0.20235	1209.7940	13.8094	6.0680	2.0935	1207.5592	1213	0.0045
Ti <sup>18+</sup>	22	0.04574	0.19264	1341.3326	16.0032	6.4032	2.3312	1338.8465	1346	0.0053
V <sup>19+</sup>	23	0.04374	0.18383	1479.6323	18.4174	6.7384	2.5817	1476.8813	1486	0.0061
Cr <sup>20+</sup>	24	0.04191	0.17579	1624.6929	21.0627	7.0737	2.8450	1621.6637	1634	0.0075
Mn <sup>21+</sup>	25	0.04022	0.16842	1776.5144	23.9495	7.4091	3.1211	1773.1935	1788	0.0083
Fe <sup>22+</sup>	26	0.03867	0.16165	1935.0968	27.0883	7.7444	3.4101	1931.4707	1950	0.0095
Co <sup>23+</sup>	27	0.03723	0.15540	2100.4398	30.4898	8.0798	3.7118	2096.4952	2119	0.0106
Ni <sup>24+</sup>	28	0.03589	0.14961	2272.5436	34.1644	8.4153	4.0264	2268.2669	2295	0.0116
Cu <sup>25+</sup>	29	0.03465	0.14424	2451.4080	38.1228	8.7508	4.3539	2446.7858	2478	0.0126

<sup>a</sup> Radius of the paired inner electrons of four-electron atoms from Eq. (10.51).<sup>b</sup> Radius of the paired outer electrons of four-electron atoms from Eq. (10.62).<sup>c</sup> Electric energy of the outer electrons of four-electron atoms from Eq. (10.63).<sup>d</sup> Magnetic energy of the outer electrons of four-electron atoms upon unpairing from Eq. (7.30) and Eq. (10.64).<sup>e</sup> Change in the velocity of the paired inner electrons due to the unpaired outer electron of four-electron atoms during ionization from Eq. (10.46).<sup>f</sup> Change in the kinetic energy of the paired inner electrons due to the unpaired outer electron of four-electron atoms during ionization from Eq. (10.47).<sup>g</sup> Calculated ionization energies of four-electron atoms from Eq. (10.68) for  $Z > 4$  and Eq. (10.66) for Be.<sup>h</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.2 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The beryllium atom isoelectronic series is given in Table 10.2 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Be isoelectronic and Rydberg series, as well as direct experimental data.

#### P-ORBITAL ELECTRONS BASED ON AN ENERGY MINIMUM

For each four-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)) and two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62). For  $Z \geq 5$ , the next electron which binds to form the corresponding five-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons such that it forms and unpaired orbitsphere at radius  $r_5$ .

The central Coulomb force,  $F_{ele}$ , acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner four electrons is given by Eq. (10.28) with the appropriate charge and radius:

$$F_{ele} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} i_r \quad (10.69)$$

for  $r > r_4$ . The same form of force equation also applies to six through ten-electron atoms as well as five-electron atoms:

$$F_{ele} = \frac{(Z-n)e^2}{4\pi\epsilon_0 r_n^2} i_r \quad (10.70)$$

for  $r > r_n$  where  $n$  corresponds to the number of electrons of the atom and  $Z$  is its atomic number. In each case, the magnetic field of the binding outer electron changes the angular velocities of the inner electrons. However, in each case, the magnetic field of the outer electron provides a central Lorentzian force which exactly balances the change in centrifugal force because of the change in angular velocity [1]. The inner electrons remain at their initial radii, but cause a diamagnetic



force according to Lenz's law.

The diamagnetic force,  $F_{\text{diamagnetic}}$ , for the formation of an s orbital given by Eq. (10.11) with the appropriate radii is

$$F_{\text{diamagnetic}} = -\frac{\hbar^2}{4m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.71)$$

However, with the formation of a third shell, a nonuniform distribution of charge is possible that achieves an energy minimum. Minimum energy configurations are given by solutions to Laplace's Equation. The general form of the solution (Eq. (11.1)) is

$$\Phi(r, \theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} B_{\ell, m} r^{-(\ell+1)} Y_{\ell}^m(\theta, \phi) \quad (10.72)$$

As shown in the Excited States of the One-Electron Atom (Quantization) section, this general solution in the form of a wave-equation gives the functions of the resonant photons of excited states. From Eqs. (2.15-2.16):

$$\begin{aligned} E_{r_{\text{photon } n, \ell, m}} &= \frac{e(na_H)^{\ell}}{4\pi\epsilon_0} \frac{1}{r^{(\ell+2)}} \left[ -Y_0^0(\theta, \phi) + \frac{1}{n} \left[ Y_0^0(\theta, \phi) + \text{Re}\{Y_{\ell}^m(\theta, \phi)e^{i\omega_n t}\} \right] \right] \delta(r - r_n) \\ \omega_n &= 0 \text{ for } m = 0 \\ n &= 1, 2, 3, 4, \dots \\ \ell &= 1, 2, \dots, n-1 \\ m &= -\ell, -\ell+1, \dots, 0, \dots, +\ell \end{aligned} \quad (10.73)$$

$E_{r_{\text{total}}}$  is the sum of the "trapped photon" and proton electric fields,

$$\begin{aligned} E_{r_{\text{total}}} &= \frac{e}{4\pi\epsilon_0 r^2} + \frac{e(na_H)^{\ell}}{4\pi\epsilon_0} \frac{1}{r^{(\ell+2)}} \left[ -Y_0^0(\theta, \phi) + \frac{1}{n} \left[ Y_0^0(\theta, \phi) + \text{Re}\{Y_{\ell}^m(\theta, \phi)e^{i\omega_n t}\} \right] \right] \delta(r - r_n) \\ \omega_n &= 0 \text{ for } m = 0 \end{aligned} \quad (10.74)$$

As shown in the Angular Function section and the Instability of Excited States section, the charge-density functions including the time-function factor are also solutions of Laplace's equation in the form of a wave-equation (Eqs. (1.48-1.49)):

$$\ell = 0$$

$$\rho(r, \theta, \phi, t) = \frac{e}{8\pi r^2} [\delta(r - r_n)] [Y_0^0(\theta, \phi) + Y_{\ell}^m(\theta, \phi)] \quad (10.75)$$

$$\ell \neq 0$$

$$\rho(r, \theta, \phi, t) = \frac{e}{4\pi r^2} [\delta(r - r_n)] \left[ Y_0^0(\theta, \phi) + \text{Re}\{Y_{\ell}^m(\theta, \phi)[1 + e^{i\omega_n t}]\} \right] \quad (10.76)$$

$$\rho(r, \theta, \phi, t) = \frac{e}{4\pi r^2} [\delta(r - r_n)] [Y_0^0(\theta, \phi) + \text{Re}\{Y_\ell^m(\theta, \phi)e^{i\omega_n t}\}] \quad (10.77)$$

where

$$\text{Re}\{Y_\ell^m(\theta, \phi)[1 + e^{i\omega_n t}]\} = \text{Re}[Y_\ell^m(\theta, \phi) + Y_\ell^m(\theta, \phi)e^{i\omega_n t}] = P_\ell^m(\cos\theta)\cos m\phi + P_\ell^m(\cos\theta)\cos(m\phi + \omega_n t)$$

or  $\text{Re}\{Y_\ell^m(\theta, \phi)e^{i\omega_n t}\} = P_\ell^m(\cos\theta)\cos(m\phi + \omega_n t)$  and to keep the form of the spherical harmonic as a traveling wave about the z-axis,  $\omega_n = m\omega_n$ . In the cases that  $m \neq 0$ , Eq. (1.65) is a traveling charge-density wave that moves on the surface of the orbitsphere about the z-axis with frequency  $\omega_n$  and modulates the orbitsphere corresponding to  $\ell = 0$ . These functions comprise the well known s, p, d, f, etc. orbitals wherein the constant function  $Y_0^0(\theta, \phi)$  corresponds to the spin function having spin angular momentum and the modulation function  $\text{Re}\{Y_\ell^m(\theta, \phi)e^{i\omega_n t}\}$  corresponds to the orbital function having orbital angular momentum as given in the Angular Function section and the Rotational Parameters of the Electron (Angular Momentum, Rotational Energy, Moment of Inertia) section.

Similar to the phenomenon observed for spherical conductors [4-5], spherical harmonic charge-density waves may be induced in the inner electron orbitspheres with the addition of one or more outer electrons, each having an orbital quantum number  $\ell \neq 0$  as given by Eq. (10.77). With  $Z > 5$ , an energy minimum is achieved when the fifth through tenth electrons of each five through ten-electron atom fills a p orbital with the formation of orthogonal complementary charge-density waves in the inner shell electrons. To maintain the symmetry of the central charge and the energy minimum condition given by solutions to Laplace's equation (Eq. (10.72)), the charge-density waves on electron orbitspheres at  $r_1$  and  $r_3$  complement those of the outer orbitals when the outer p orbitals are not all occupied by at least one electron, and the complementary charge-density waves are provided by electrons at  $r_3$  when this condition is met. Since the angular harmonic charge-density waves are nonradiative as shown in the Spacetime Fourier Transform of the Electron Function section and Appendix I: Nonradiation Based on the Electromagnetic Fields and the Poynting Power Vector, the time-averaged central field is inverse  $r$ -squared even though the central field is modulated by the concentric charge-density waves. The modulated central field maintains the spherical harmonic orbitals that maintain the spherical-harmonic phase according to Eq. (10.72). For  $\ell=1$  and  $m=\pm 1$ , the spherical harmonics  $Y_\ell^m(\theta, \phi)$  given by Eqs. (1.66-1.67) are

$$Y_{1,x} = \sin\theta \cos\phi \quad (10.78)$$

$$Y_{1,y} = \sin\theta \sin\phi \quad (10.79)$$

wherein the  $x$  and  $y$  designation corresponds, respectively, to the historical  $p_x$  and  $p_y$  probability-density functions of quantum mechanics. The  $p_x$  and  $p_y$  charge-density waves rotate in the same direction such that their individual contributions to the diamagnetic force add, or they rotate in opposite directions such that their contributions cancel. In addition, for  $\ell=1$  and  $m=0$ , the spherical harmonic  $Y_\ell^m(\theta, \phi)$  is

$$Y_{1,0} = \cos \theta \quad (10.80)$$

wherein the  $z$  designation corresponds to the historical  $p_z$  probability-density function of quantum mechanics. The demonstration that the modulated orbitsphere solutions are solutions of the wave equation appears in Box 1.1.

As shown by Eq. (10.9), the diamagnetic force is dependent on the integral of the charge-density squared over the surface of the orbitsphere with the further constant of the invariance of charge under Gauss's integral law. The correction to the force due to a time and spatially-dependent spherical harmonic current-density wave is given by the normalization term for spherical harmonics given by Eq. (3.53) of Jackson [6] and Eq. (6-76) of McQuarrie [7]:

$$\frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \quad (10.81)$$

Since the spin function is constant and the orbital function is a traveling wave, only the latter contributes to the diamagnetic and paramagnetic-force contributions of an unpaired electron. Substitution of Eq. (10.81) into Eq. (10.11) gives the contribution of each orbital to the diamagnetic force,  $F_{\text{diamagnetic}}$ , which is summed over the orbitals:

$$F_{\text{diamagnetic}} = - \sum_m \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^2}{4m_e r_n^2 r_s} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.82)$$

where the contributions from orbitals having  $|m|=1$  add positively or negatively.

For each five-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62), and an unpaired electron is in an orbitsphere at  $r_5$  given by Eq. (10.113). For  $Z \geq 6$ , the next electron which binds to form the corresponding six-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-pairing force to form a filled  $s$  orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (10.71) with the radius  $r_6$ ) reduces the

energy of the atom less than that due to the alternative forces on two unpaired p electrons in an orbitsphere at the same radius  $r_0$ .

In general, a nonuniform distribution of charge achieves an energy minimum with the formation of a third shell due to the dependence of the magnetic forces on the nuclear charge and orbital energy (Eqs. (10.52), (10.55), and (10.93)). The outer electrons of atoms and ions that are isoelectronic with the series boron through neon half-fill a 2p level with unpaired electrons at nitrogen, then fill the level with paired electrons at neon. *Thus, it is found that the purely postulated Hund's Rule and the Pauli Exclusion Principle of the assignment of unique quantum numbers to all electrons are not "weird spooky action" phenomena unique to quantum mechanics that require all electrons in the universe to have instantaneous communication and coordination with no basis in physical laws such as Maxwell's equations. Rather they are phenomenological consequences of those laws.*

Each outer 2p electron contributes spin as well as orbital angular momentum. The former gives rise to spin pairing to another 2p electron when an energy minimum is achieved. The corresponding force,  $F_{mag2}$ , given by Eq. (10.52) is:

$$F_{mag2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} i_r \quad (10.83)$$

The orbital angular momenta of spin-paired electrons may add to double the spin-pairing force of each individual p electron such that the resultant force is four times that of Eq. (10.83) in agreement with the energy (and force) relationship of magnetic fields (Eq. (1.122)):

$$F_{mag2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} i_r \quad (10.84)$$

Or, the orbital angular momenta of spin-paired electrons may add negatively to cancel such that  $F_{mag2}$  due to the contribution from spin-pairing alone is equivalent to that given by Eq. (10.83).

Since the electron velocity given by Eq. (1.47) is

$$v_n = \frac{\hbar}{m_e r_n} \quad (10.85)$$

The scalar sum of the magnitude of the angular momentum of each infinitesimal point of the orbitsphere  $L_i$  of mass  $m_i$  must be constant. The constant is  $\hbar$ .

$$\sum |L_i| = \sum |\mathbf{r} \times m_i \mathbf{v}| = m_e r_n \frac{\hbar}{m_e r_n} = \hbar \quad (10.86)$$

where the velocity is given by Eq. (1.47). The sum of the magnitude of the angular momentum of the electron is  $\hbar$  in any inertial frame and is relativistically invariant. The vector projections of the orbitsphere spin

angular momentum relative to the Cartesian coordinates are given in the Spin Angular Momentum of the Orbitsphere with  $l = 0$  section. The orbital and spin angular momentum of excited states is also quantized in units of  $\hbar$  as shown in the Orbital and Spin Splitting section. The orbital moment of inertia,  $I_{orbital}$ , corresponding to orbital quantum number  $\ell$  (Eq. (1.96)) is

$$I_{orbital} = m_e r_n^2 \left[ \frac{\ell(\ell+1)}{\ell^2 + 2\ell + 1} \right]^{\frac{1}{2}} = m_e r_n^2 \sqrt{\frac{\ell}{\ell+1}} \quad (10.87)$$

The spin and orbital angular momentum can superimpose positively or negatively:

$$L_{z\ total} = L_{z\ spin} + L_{z\ orbital} \quad (10.88)$$

Thus, the contribution of the orbital angular momentum to the paramagnetic force is also that given by Eq. (10.83):

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.89)$$

And, the total force is given as the sum over the orbital and spin angular momenta that may add positively or negatively to achieve an energy minimum while maintaining the conservation of angular momentum.

The amplitude of the corresponding rotational energy,  $E_{rotational\ orbital}$ , given by Eqs. (1.95-1.96) is

$$E_{rotational\ orbital} = \frac{\hbar^2}{2m_e r_n^2} \left[ \frac{\ell(\ell+1)}{\ell^2 + 2\ell + 1} \right]^{\frac{1}{2}} = \frac{\hbar^2}{2m_e r_n^2} \sqrt{\frac{\ell}{\ell+1}} \quad (10.90)$$

Since the orbital rotational energy arises from a spin function (spin angular momentum) modulated by a spherical harmonic angular function (orbital angular momentum), the time-averaged orbital rotational energy having an amplitude given by Eq. (1.95) (Eq. (10.90)) is zero:

$$\langle E_{rotational\ orbital} \rangle = 0 \quad (10.91)$$

However, the orbital energy is nonzero in the presence of a magnetic field.

N-electron atoms having  $Z > n$  possess an electric field of

$$\mathbf{E} = \frac{(Z-n)e}{4\pi\epsilon_0 r^2} \mathbf{i}_r \quad (10.92)$$

for  $r > r_n$ . Since there is a source of dissipative,  $\mathbf{J} \cdot \mathbf{E}$  of Eq. (10.27), the magnetic moments of the inner electrons may change due to the outer electron such that the energy of the n-electron atom is lowered. The diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , due to a relativistic effect with an electric field for  $r > r_n$  (Eq. (10.35)) is dependent on the amplitude of the orbital energy. Using the orbital energy with  $\ell=1$  (Eq. (10.90)), the energy

$m_e \Delta v^2$  of Eq. (10.29) is reduced by the factor of  $\left(1 - \frac{\sqrt{2}}{2}\right)$  due to the contribution of the charge-density wave of the inner electrons at  $r_3$ . Thus,  $F_{\text{diamagnetic2}}$  is given by

$$F_{\text{diamagnetic2}} = - \left[ \frac{Z - n}{Z - (n - 1)} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{m_e r_n^4} 10 \sqrt{s(s+1)} \hat{r} \quad (10.93)$$

Using the forces given by Eqs. (10.70), (10.82-10.84), (10.89), (10.93), and the radii  $r_3$  given by Eq. (10.62), the radii of the 2p electrons of all five through ten-electron atoms may be solved exactly. The electric energy given by Eq. (10.102) gives the corresponding exact ionization energies.  $F_{\text{ele}}$  and  $F_{\text{diamagnetic2}}$  given by Eqs. (10.70) and (10.93), respectively, are of the same form for all atoms with the appropriate nuclear charges and atomic radii.  $F_{\text{diamagnetic}}$  given by Eq. (10.82) and  $F_{\text{mag2}}$  given by Eqs. (10.83-10.84) and (10.89) are of the same form with the appropriate factors that depend on the minimum-energy electron configuration. The general equation and the summary of the parameters that determine the exact radii and ionization energies of all five through ten-electron atoms are given the General Equation For The Ionization Energies of Five Through Ten-Electron Atoms section and in Table 10.9.

## FIVE-ELECTRON ATOMS

Five-electron atoms can be solved exactly using the results of the solutions of one, two, three, and four-electron atoms.

## RADIUS AND IONIZATION ENERGY OF THE OUTER ELECTRON OF THE BORON ATOM

For each four-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)) and two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62). For  $Z \geq 5$ , the next electron which binds to form the corresponding five-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons such that it forms an unpaired orbitsphere at radius  $r_5$ . The resulting electron configuration is  $1s^2 2s^2 2p^1$ , and the orbital arrangement is

2p state

$$\begin{array}{ccc} \uparrow & \_ & \_ \\ 1 & 0 & -1 \end{array}$$

(10.94)

corresponding to the ground state  $^2P_{1/2}^0$ .

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} \mathbf{i}_r \quad (10.95)$$

for  $r > r_4$ .

The single p orbital of the boron atom produces a diamagnetic force equivalent to that of the formation of an s orbital due to the induction of complementary and spherically symmetrical charge-density waves on electron orbitspheres at  $r_1$  and  $r_3$  in order to achieve a solution of Laplace's equation (Eq. (10.72)). The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is two times that of Eqs. (10.11) and (10.71) since the two electrons at  $r_1 = r_2$  act on the two electrons at  $r_3 = r_4$  which in turn act of the outer electron.  $\mathbf{F}_{diamagnetic}$  is also given by Eq. (10.82) with the appropriate radii when the contributions from the three orthogonal spherical harmonics are summed over including those induced:

$$\mathbf{F}_{diamagnetic} = -\frac{2\hbar^2}{4m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.96)$$

The charge induction forms complementary mirror charge-density waves which must have opposing angular momenta such that momentum is conserved. In this case,  $\mathbf{F}_{mag2}$  given by Eq. (10.89) is zero:

$$\mathbf{F}_{mag2} = 0 \quad (10.97)$$

The outward centrifugal force on electron 5 is balanced by the electric force and the magnetic force (on electron 5). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.95)) and diamagnetic (Eq. (10.96)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} - \frac{2\hbar^2}{4m_e r_5^2 r_3} \sqrt{s(s+1)} \quad (10.98)$$

Substitution of  $v_5 = \frac{\hbar}{m_e r_5}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.98) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} - \frac{\hbar^2}{2m_e r_5^2 r_3} \sqrt{\frac{3}{4}} \quad (10.99)$$

$$r_5 = \frac{a_0}{\left[ (Z-4) - \frac{\sqrt{3}}{2r_3} \right]}, \quad r_3 \text{ in units of } a_0 \quad (10.100)$$

Substitution of  $\frac{r_3}{a_0} = 1.07930$  (Eq. (10.62) with  $Z = 5$ ) into Eq. (10.100) gives

$$r_3 = 1.67000351a_0 \quad (10.101)$$

In general, the energy stored in the electric field,  $E(electric)$ , is given by Eq. (10.43) with the appropriate charge and radius:

$$E(electric) = -\frac{(Z-(n-1))e^2}{8\pi\epsilon_0 r_n} \quad (10.102)$$

where  $n$  corresponds to the number of electrons of the atom and  $Z$  is its atomic number. The ionization energy is given by the sum of the electric energy and the energy corresponding to the change in magnetic-moments of the inner shell electrons. Since there is no source of dissipative power,  $\mathbf{J} \cdot \mathbf{E}$  of Eq. (10.27), to compensate for any potential change in the magnetic moments,  $\Delta m$ , of the inner electrons due to the ionization of an outer electron of the boron atom, there is a diamagnetic energy term in the ionization energy for this atom that follows from the corresponding term for the lithium atom. Since the diamagnetic force for the boron atom (Eq. (10.96)) is twice that of the corresponding force (Eq. (10.11)) of the lithium atom, this term is given by twice that of Eqs. (10.15-10.24), with  $Z = 5$ ,  $r_3$  given by Eq. (10.62), and  $r_3$  given by Eq. (10.101). Thus, the change in magnetic energy of the inner orbitsphere at  $r_3$  is 85.429321 %, so that the corresponding energy  $\Delta E_{mag}$  is

$$\Delta E_{mag} = 2(0.85429321 \text{ eV} \times 0.09100214 \text{ eV}) = 0.15548501 \text{ eV} \quad (10.103)$$

where the magnetic energy of the inner electrons is 0.09100214 eV (Eqs. (10.64) and (10.101)). Then, the ionization energy of the boron atom is given by Eqs. (10.101-10.102) and (10.103):

$$\begin{aligned} E(\text{ionization}; B) &= \frac{(Z-4)e^2}{8\pi\epsilon_0 r_3} + \Delta E_{mag} \\ &= 8.147170901 \text{ eV} + 0.15548501 \text{ eV} = 8.30265592 \text{ eV} \end{aligned} \quad (10.104)$$

The experimental ionization energy of the boron atom is 8.29803 eV [3].

#### THE IONIZATION ENERGIES OF FIVE-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 5$

Five-electron atoms having  $Z > 5$  possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that  $F_{diamagnetic}$  is minimized while  $F_{mag2}$  is maximized. From Eq. (10.82), the diamagnetic force,  $F_{diamagnetic}$ , is given by the sum of the contributions from the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals corresponding to  $m = 1, -1$ , and 0, respectively:



$$\mathbf{F}_{\text{diamagnetic}} = -\left(\frac{2}{3} + \frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_s^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_s^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.105)$$

With  $Z > 5$ , the charge induction forms complementary mirror charge-density waves such that the angular momenta do not cancel. From Eq. (10.89),  $\mathbf{F}_{\text{mag}2}$  corresponding to the orbital angular momentum of the single  $p_x$  electron is

$$\mathbf{F}_{\text{mag}2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_s^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.106)$$

The second diamagnetic force,  $\mathbf{F}_{\text{diamagnetic}2}$ , due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$\mathbf{F}_{\text{diamagnetic}2} = -\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_s^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (10.107)$$

In the case that  $Z > 5$ , the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.95)) and diamagnetic (Eqs. (10.105) and (10.107)), and paramagnetic (Eq. (10.106)) forces as follows:

$$\frac{m_e v_s^2}{r_s} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_s^2} - \frac{5\hbar^2}{12m_e r_s^2 r_3} \sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_s^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_s^4 m_e} 10 \sqrt{s(s+1)} \quad (10.108)$$

Substitution of  $v_s = \frac{\hbar}{m_e r_s}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.108) gives:

$$\frac{\hbar^2}{m_e r_s^3} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_s^2} - \frac{5\hbar^2}{12m_e r_s^2 r_3} \sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_s^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_s^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (10.109)$$

The quadratic equation corresponding to Eq. (10.109) is

$$\left(\frac{(Z-4)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{1}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right) r_s^2 - \frac{\hbar^2}{m_e} r_s - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e} 10 \sqrt{\frac{3}{4}} = 0 \quad (10.110)$$

$$r_s^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-4)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{1}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} r_s - \frac{\frac{\hbar^2}{m_e} \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3 10 \sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{1}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} = 0 \quad (10.111)$$

The solution of Eq. (10.111) using the quadratic formula is:

$$r_3 = \frac{\left( \frac{\hbar^2}{m_e} - \left( \frac{(Z-4)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{1}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) \right) \pm \sqrt{\left( \frac{\hbar^2}{m_e} - \left( \frac{(Z-4)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{1}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) \right)^2 + 4 \left( \frac{\hbar^2}{m_e} \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}} \right)}}{2} \quad (10.112)$$

$$r_3 = \frac{\left( \frac{a_0}{(Z-4) - \left( \frac{5}{24} - \frac{1}{2Z} \right) \frac{\sqrt{3}}{r_3}} \right) \pm a_0 \sqrt{\left( \frac{1}{(Z-4) - \left( \frac{5}{24} - \frac{1}{2Z} \right) \frac{\sqrt{3}}{r_3}} \right)^2 + 20\sqrt{3} \left( \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}}{2} \quad (10.113)$$

$r_3$  in units of  $a_0$

where  $r_3$  is given by Eq. (10.62). The positive root of Eq. (10.113) must be taken in order that  $r_3 > 0$ . The radii of several five-electron atoms are given in Table 10.3.

The ionization energies for the five-electron atoms with  $Z > 5$  are given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radii,  $r_3$ , given by Eq. (10.113)):

$$E(\text{Ionization}) = -\text{Electric Energy} = \frac{(Z-4)e^2}{8\pi\epsilon_0 r_3} \quad (10.114)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured five-electron atoms are given in Table 10.3.

Table 10.3. Ionization energies for some five-electron atoms.

5 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_2$ ( $a_0$ ) <sup>b</sup>	$r_3$ ( $a_0$ ) <sup>c</sup>	Theoretical Ionization Energies <sup>d</sup> (eV)	Experimental Ionization Energies <sup>e</sup> (eV)	Relative Error
B	5	0.20670	1.07930	1.67000	8.30266	8.29803	-0.00056
C <sup>+</sup>	6	0.17113	0.84317	1.12092	24.2762	24.38332	0.0044
N <sup>2+</sup>	7	0.14605	0.69385	0.87858	46.4585	47.44924	0.0209
O <sup>3+</sup>	8	0.12739	0.59020	0.71784	75.8154	77.41353	0.0206
F <sup>4+</sup>	9	0.11297	0.51382	0.60636	112.1922	114.2428	0.0179
Ne <sup>5+</sup>	10	0.10149	0.45511	0.52486	155.5373	157.93	0.0152
Na <sup>6+</sup>	11	0.09213	0.40853	0.46272	205.8266	208.5	0.0128
Mg <sup>7+</sup>	12	0.08435	0.37065	0.41379	263.0469	265.96	0.0110
Al <sup>8+</sup>	13	0.07778	0.33923	0.37425	327.1901	330.13	0.0089
Si <sup>9+</sup>	14	0.07216	0.31274	0.34164	398.2509	401.37	0.0078
P <sup>10+</sup>	15	0.06730	0.29010	0.31427	476.2258	479.46	0.0067
S <sup>11+</sup>	16	0.06306	0.27053	0.29097	561.1123	564.44	0.0059
Cl <sup>12+</sup>	17	0.05932	0.25344	0.27090	652.9086	656.71	0.0058
Ar <sup>13+</sup>	18	0.05599	0.23839	0.25343	751.6132	755.74	0.0055
K <sup>14+</sup>	19	0.05302	0.22503	0.23808	857.2251	861.1	0.0045
Ca <sup>15+</sup>	20	0.05035	0.21308	0.22448	969.7435	974	0.0044
Sc <sup>16+</sup>	21	0.04794	0.20235	0.21236	1089.1678	1094	0.0044
Ti <sup>17+</sup>	22	0.04574	0.19264	0.20148	1215.4975	1221	0.0045
V <sup>18+</sup>	23	0.04374	0.18383	0.19167	1348.7321	1355	0.0046
Cr <sup>19+</sup>	24	0.04191	0.17579	0.18277	1488.8713	1496	0.0048
Mn <sup>20+</sup>	25	0.04022	0.16842	0.17466	1635.9148	1644	0.0049
Fe <sup>21+</sup>	26	0.03867	0.16165	0.16724	1789.8624	1799	0.0051
Co <sup>22+</sup>	27	0.03723	0.15540	0.16042	1950.7139	1962	0.0058
Ni <sup>23+</sup>	28	0.03589	0.14961	0.15414	2118.4690	2131	0.0059
Cu <sup>24+</sup>	29	0.03465	0.14424	0.14833	2293.1278	2308	0.0064

<sup>a</sup> Radius of the first set of paired inner electrons of five-electron atoms from Eq. (10.51).<sup>b</sup> Radius of the second set of paired inner electrons of five-electron atoms from Eq. (10.62).<sup>c</sup> Radius of the outer electron of five-electron atoms from Eq. (10.113) for  $Z > 5$  and Eq. (10.101) for  $B$ .<sup>d</sup> Calculated ionization energies of five-electron atoms given by the electric energy (Eq. (10.114)) for  $Z > 5$  and Eq. (10.104) for  $B$ .<sup>e</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.3 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray spectroscopy. In this case, the experimental capability is three to four

significant figures which is consistent with the last column. The boron atom isoelectronic series is given in Table 10.3 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of B isoelectronic and Rydberg series, as well as direct experimental data.

### SIX-ELECTRON ATOMS

Six-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, and five-electron atoms.

### RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE CARBON ATOM

For each five-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62), and an unpaired electron is in an orbitsphere at  $r_5$  given by Eq. (10.113). For  $Z \geq 6$ , the next electron which binds to form the corresponding six-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-pairing force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (10.71) with the radius  $r_6$ ) reduces the energy of the atom less than that due to the alternative forces on two unpaired p electrons in an orbitsphere at the same radius  $r_6$ . The resulting electron configuration is  $1s^2 2s^2 2p^2$ , and the orbital arrangement is

$$\begin{array}{ccc} \text{2p state} & & \\ \uparrow & \uparrow & \_ \\ 1 & 0 & -1 \end{array} \quad (10.115)$$

corresponding to the ground state  $^3P_0$ .

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$F_{ele} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} \mathbf{i}_r \quad (10.116)$$

for  $r > r_3$ .

The two orthogonal electrons form charge-charge density waves such that the total angular momentum of the two outer electrons is conserved which determines the diamagnetic force according to Eq. (10.82).  $F_{\text{diamagnetic}}$  is

$$F_{\text{diamagnetic}} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \hat{i}_r \quad (10.117)$$

corresponding to  $m = 1$ .

The charge induction forms complementary mirror charge-density waves which must have opposing angular momenta such that momentum is conserved. In this case,  $F_{\text{mag}2}$  given by Eq. (10.89) is zero:

$$F_{\text{mag}2} = 0 \quad (10.118)$$

The outward centrifugal force on electron 6 is balanced by the electric force and the magnetic forces (on electron 6). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.116)) and diamagnetic (Eq. (10.117)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{\hbar^2}{6m_e r_6^2 r_3} \sqrt{s(s+1)} \quad (10.119)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.119) gives:

$$\frac{\hbar^2}{m_e r_6^3} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{\hbar^2}{6m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \quad (10.120)$$

$$r_6 = \frac{a_0}{\left[ (Z-5) - \frac{\sqrt{3}}{6r_3} \right]}, \quad r_3 \text{ in units of } a_0 \quad (10.121)$$

Substitution of  $\frac{r_3}{a_0} = 0.84317$  (Eq. (10.62) with  $Z=6$ ) into Eq. (10.121) gives

$$r_6 = 1.20654a_0 \quad (10.122)$$

The ionization energy of the carbon atom is given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radius,  $r_6$ , given by Eq. (10.122)):

$$E(\text{ionization}; C) = -\text{Electric Energy} = \frac{(Z-5)e^2}{8\pi\epsilon_0 r_6} = 11.27671 \text{ eV} \quad (10.123)$$

where  $r_6 = 1.20654a_0$  (Eq. (10.122)) and  $Z=6$ . The experimental ionization energy of the carbon atom is 11.2603 eV [3].

### THE IONIZATION ENERGIES OF SIX-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 6$

Six-electron atoms having  $Z > 6$  possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that  $F_{\text{diamagnetic}}$  is minimized while  $F_{\text{mag}2}$  is maximized. From Eq. (10.82), the diamagnetic force,  $F_{\text{diamagnetic}}$ , is given by the sum of the contributions from the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals corresponding to  $m = 1, -1$ , and  $0$ , respectively:

$$F_{\text{diamagnetic}} = -\left(\frac{2}{3} + \frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.124)$$

With  $Z > 6$ , the charge induction forms complementary mirror charge-density waves such that the angular momenta do not cancel. From Eq. (10.89),  $F_{\text{mag}2}$  corresponding to the orbital angular momentum of the two p electrons in addition to complementary charge-density waves is

$$F_{\text{mag}2} = 2 \frac{1}{Z} \frac{2\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{4\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.125)$$

The second diamagnetic force,  $F_{\text{diamagnetic}2}$ , due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$F_{\text{diamagnetic}2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (10.126)$$

In the case that  $Z > 6$ , the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.116)), diamagnetic (Eqs. (10.124) and (10.126)), and paramagnetic (Eq. (10.125)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{5\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{4\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \quad (10.127)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.127) gives:

$$\frac{\hbar^2}{m_e r_6^3} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{5\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{4\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (10.128)$$

The quadratic equation corresponding to Eq. (10.128) is

$$\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{4}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right) r_6^2 - \frac{\hbar^2}{m_e} r_6 - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e} 10 \sqrt{\frac{3}{4}} = 0 \quad (10.129)$$

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{4}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3 10 \sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{4}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} = 0 \quad (10.130)$$

The solution of Eq. (10.130) using the quadratic formula is:

$$r_6 = \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{4}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} \pm \frac{\sqrt{\left(\frac{\hbar^2}{m_e}\right)^2 - 4 \left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{4}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right) \frac{\hbar^2}{m_e} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3 10 \sqrt{\frac{3}{4}}}}{2} \quad (10.131)$$

$$r_6 = \frac{\frac{a_0}{\left((Z-5) - \left(\frac{5}{24} - \frac{2}{Z}\right)\frac{\sqrt{3}}{r_3}\right)} \pm a_0}{2} \sqrt{\frac{1}{\left((Z-5) - \left(\frac{5}{24} - \frac{2}{Z}\right)\frac{\sqrt{3}}{r_3}\right)} + \frac{20\sqrt{3} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3}{\left((Z-5) - \left(\frac{5}{24} - \frac{2}{Z}\right)\frac{\sqrt{3}}{r_3}\right)}} \quad (10.132)$$

$r_3$  in units of  $a_0$

where  $r_3$  is given by Eq. (10.62). The positive root of Eq. (10.132) must be taken in order that  $r_6 > 0$ . The final radius of electron 6,  $r_6$ , is given by Eq. (10.132); this is also the final radius of electron 5. The radii of several six-electron atoms are given in Table 10.4.

The ionization energies for the six-electron atoms with  $Z > 6$  are given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radii  $r_6$ , given by Eq. (10.132)):

$$E(\text{ionization}) = -\text{Electric Energy} = \frac{(Z-5)e^2}{8\pi\epsilon_0 r_6} \quad (10.133)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured six-electron atoms are

given in Table 10.4.

Table 10.4. Ionization energies for some six-electron atoms.

6 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_3$ ( $a_0$ ) <sup>b</sup>	$r_6$ ( $a_0$ ) <sup>c</sup>	Theoretical Ionization Energies <sup>d</sup> (eV)	Experimental Ionization Energies <sup>e</sup> (eV)	Relative Error
C	6	0.17113	0.84317	1.20654	11.27671	11.2603	-0.0015
N <sup>+</sup>	7	0.14605	0.69385	0.90119	30.1950	29.6013	-0.0201
O <sup>2+</sup>	8	0.12739	0.59020	0.74776	54.5863	54.9355	0.0064
F <sup>3+</sup>	9	0.11297	0.51382	0.63032	86.3423	87.1398	0.0092
Ne <sup>4+</sup>	10	0.10149	0.45511	0.54337	125.1986	126.21	0.0080
Na <sup>5+</sup>	11	0.09213	0.40853	0.47720	171.0695	172.18	0.0064
Mg <sup>6+</sup>	12	0.08435	0.37065	0.42534	223.9147	225.02	0.0049
Al <sup>7+</sup>	13	0.07778	0.33923	0.38365	283.7121	284.66	0.0033
Si <sup>8+</sup>	14	0.07216	0.31274	0.34942	350.4480	351.12	0.0019
P <sup>9+</sup>	15	0.06730	0.29010	0.32081	424.1135	424.4	0.0007
S <sup>10+</sup>	16	0.06306	0.27053	0.29654	504.7024	504.8	0.0002
Cl <sup>11+</sup>	17	0.05932	0.25344	0.27570	592.2103	591.99	-0.0004
Ar <sup>12+</sup>	18	0.05599	0.23839	0.25760	686.6340	686.1	-0.0008
K <sup>13+</sup>	19	0.05302	0.22503	0.24174	787.9710	786.6	-0.0017
Ca <sup>14+</sup>	20	0.05035	0.21308	0.22772	896.2196	894.5	-0.0019
Sc <sup>15+</sup>	21	0.04794	0.20235	0.21524	1011.3782	1009	-0.0024
Ti <sup>16+</sup>	22	0.04574	0.19264	0.20407	1133.4456	1131	-0.0022
V <sup>17+</sup>	23	0.04374	0.18383	0.19400	1262.4210	1260	-0.0019
Cr <sup>18+</sup>	24	0.04191	0.17579	0.18487	1398.3036	1396	-0.0017
Mn <sup>19+</sup>	25	0.04022	0.16842	0.17657	1541.0927	1539	-0.0014
Fe <sup>20+</sup>	26	0.03867	0.16165	0.16899	1690.7878	1689	-0.0011
Co <sup>21+</sup>	27	0.03723	0.15540	0.16203	1847.3885	1846	-0.0008
Ni <sup>22+</sup>	28	0.03589	0.14961	0.15562	2010.8944	2011	0.0001
Cu <sup>23+</sup>	29	0.03465	0.14424	0.14970	2181.3053	2182	0.0003

<sup>a</sup> Radius of the first set of paired inner electrons of six-electron atoms from Eq. (10.51).

<sup>b</sup> Radius of the second set of paired inner electrons of six-electron atoms from Eq. (10.62).

<sup>c</sup> Radius of the two unpaired outer electrons of six-electron atoms from Eq. (10.132) for  $Z > 6$  and Eq. (10.122) for C.

<sup>d</sup> Calculated ionization energies of six-electron atoms given by the electric energy (Eq. (10.133)).

<sup>e</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.4 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray



spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The carbon atom isoelectronic series is given in Table 10.4 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of C isoelectronic and Rydberg series, as well as direct experimental data.

#### SEVEN-ELECTRON ATOMS

Seven-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, and six-electron atoms.

#### RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE NITROGEN ATOM

For each six-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62), and two unpaired electrons is in an orbitsphere at  $r_6$  given by Eq. (10.132). For  $Z \geq 7$ , the next electron which binds to form the corresponding seven-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-pairing force is also possible, but the force due to the spin-pairing of the electrons (Eq. (10.71) with the radius  $r_7$ ) reduces the energy of the atom less than that due to the alternative forces on three unpaired p electrons in an orbitsphere at the same radius  $r_7$ . The resulting electron configuration is  $1s^2 2s^2 2p^3$ , and the orbital arrangement is

$$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array} \quad (10.134)$$

corresponding to the ground state  $^4S_{3/2}^0$ .

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner six electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$F_{ele} = \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} \hat{r} \quad (10.135)$$

for  $r > r_6$ .

The energy is minimized with conservation of angular momentum when the angular momenta of the two orthogonal  $p_x$  and  $p_y$  electrons cancel such that the diamagnetic force (Eq. (10.82)),  $F_{\text{diamagnetic}}$ , is

$$F_{\text{diamagnetic}} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_7^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r, \quad (10.136)$$

corresponding to  $m = 0$ .

From Eq. (10.89),  $F_{\text{mag}2}$  corresponding to the orbital angular momentum of the  $p_z$  electron is

$$F_{\text{mag}2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_7^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r, \quad (10.137)$$

The outward centrifugal force on electron 7 is balanced by the electric force and the magnetic forces (on electron 7). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.135)), diamagnetic (Eq. (10.136)), and paramagnetic (Eq. (10.137)) forces as follows:

$$\frac{m_e v_7^2}{r_7} = \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} - \frac{\hbar^2}{12m_e r_7^2 r_3} \sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_7^2 r_3} \sqrt{s(s+1)} \quad (10.138)$$

Substitution of  $v_7 = \frac{\hbar}{m_e r_7}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.138) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} - \frac{\hbar^2}{12m_e r_7^2 r_3} \sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_7^2 r_3} \sqrt{\frac{3}{4}} \quad (10.139)$$

$$r_7 = \frac{\frac{\hbar^2}{m_e}}{\frac{(Z-6)e^2}{4\pi\epsilon_0} - \frac{\hbar^2}{12m_e r_3} \sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_3} \sqrt{\frac{3}{4}}} \quad (10.140)$$

$$r_7 = \frac{a_0}{(Z-6) - \left(\frac{1}{12} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_3}}, \quad r_3 \text{ in units of } a_0 \quad (10.141)$$

Substitution of  $\frac{r_3}{a_0} = 0.69385$  (Eq. (10.62) with  $Z=7$ ) into Eq. (10.141)

gives

$$r_7 = 0.93084a_0 \quad (10.142)$$

The ionization energy of the nitrogen atom is given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radius,  $r_7$ , given by Eq. (10.142)):

$$E(\text{ionization}; N) = -\text{Electric Energy} = \frac{(Z-6)e^2}{8\pi\epsilon_0 r_7} = 14.61664 \text{ eV} \quad (10.143)$$

where  $r_7 = 0.93084a_0$  (Eq. (10.142)) and  $Z = 7$ . The experimental ionization energy of the nitrogen atom is 14.53414 eV [3].

### THE IONIZATION ENERGIES OF SEVEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 7$

Seven-electron atoms having  $Z > 7$  possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that  $F_{\text{diamagnetic}}$  is minimized while  $F_{\text{mag}2}$  is maximized. From Eq. (10.82), the diamagnetic force,  $F_{\text{diamagnetic}}$ , is given by the sum of the contributions from the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals corresponding to  $m = 1, -1$ , and 0, respectively:

$$F_{\text{diamagnetic}} = -\left(\frac{2}{3} + \frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_7^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_7^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.144)$$

With  $Z > 6$ , the charge induction forms complementary mirror charge-density waves such that the angular momenta do not cancel. From Eq. (10.89),  $F_{\text{mag}2}$  corresponding to the orbital angular momentum of the three p electrons in addition complementary charge-density waves is

$$F_{\text{mag}2} = 2 \frac{1}{Z} \frac{3\hbar^2}{m_e r_7^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.145)$$

The second diamagnetic force,  $F_{\text{diamagnetic}2}$ , due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$F_{\text{diamagnetic}2} = -\left[\frac{Z-7}{Z-6}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_7^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (10.146)$$

In the case that  $Z > 7$ , the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.135)), diamagnetic (Eqs. (10.10.144) and (10.146)), and paramagnetic (Eq. (10.145)) forces as follows:

$$\frac{m_e v_7^2}{r_7} = \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} - \frac{5\hbar^2}{12m_e r_7^2 r_3} \sqrt{s(s+1)} + \frac{6\hbar^2}{Zm_e r_7^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-7}{Z-6}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_7^4} 10 \sqrt{s(s+1)} \quad (10.147)$$

Substitution of  $v_7 = \frac{\hbar}{m_e r_7}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.147) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} - \frac{5\hbar^2}{12m_e r_7^2 r_3} \sqrt{\frac{3}{4}} + \frac{6\hbar^2}{Zm_e r_7^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-7}{Z-6}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_7^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (10.148)$$

The quadratic equation corresponding to Eq. (10.148) is

$$\left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) r_7^2 - \frac{\hbar^2}{m_e} r_7 - \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{m_e} 10 \sqrt{\frac{3}{4}} = 0 \quad (10.149)$$

$$r_7^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_7 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (10.150)$$

The solution of Eq. (10.150) using the quadratic formula is:

$$r_7 = \frac{\frac{\hbar^2}{m_e} \left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) \pm \sqrt{\left( \frac{\hbar^2}{m_e} \left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) \right)^2 + 4 \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}} \left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)}}{2} \quad (10.151)$$

$$r_7 = \frac{\frac{a_0}{\left( (Z-6) - \left( \frac{5}{24} - \frac{3}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \pm a_0 \sqrt{\left( \frac{1}{\left( (Z-6) - \left( \frac{5}{24} - \frac{3}{Z} \right) \frac{\sqrt{3}}{r_3} \right) \right)^2 + \frac{20\sqrt{3} \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-6) - \left( \frac{5}{24} - \frac{3}{Z} \right) \frac{\sqrt{3}}{r_3} \right)}}}{2} \quad (10.152)$$

$r_3$  in units of  $a_0$

where  $r_3$  is given by Eq. (10.62). The positive root of Eq. (10.152) must be taken in order that  $r_7 > 0$ . The final radius of electron 7,  $r_7$ , is given by Eq. (10.152); this is also the final radius of electrons 5 and 6. The radii of several seven-electron atoms are given in Table 10.5.

The ionization energies for the seven-electron atoms with  $Z > 7$  are given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radii,  $r_7$ , given by Eq. (10.152)):

$$E(\text{Ionization}) = - \text{Electric Energy} = \frac{(Z-6)e^2}{8\pi\epsilon_0 r_7} \quad (10.153)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured seven-electron atoms are given in Table 10.5.

Table 10.5. Ionization energies for some seven-electron atoms.

7 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_3$ ( $a_0$ ) <sup>b</sup>	$r_7$ ( $a_0$ ) <sup>c</sup>	Theoretical Ionization Energies <sup>d</sup> (eV)	Experimental Ionization Energies <sup>e</sup> (eV)	Relative Error
N	7	0.14605	0.69385	0.93084	14.61664	14.53414	-0.0057
O <sup>+</sup>	8	0.12739	0.59020	0.78489	34.6694	35.1173	0.0128
F <sup>2+</sup>	9	0.11297	0.51382	0.67084	60.8448	62.7084	0.0297
Ne <sup>3+</sup>	10	0.10149	0.45511	0.57574	94.5279	97.12	0.0267
Na <sup>4+</sup>	11	0.09213	0.40853	0.50250	135.3798	138.4	0.0218
Mg <sup>5+</sup>	12	0.08435	0.37065	0.44539	183.2888	186.76	0.0186
Al <sup>6+</sup>	13	0.07778	0.33923	0.39983	238.2017	241.76	0.0147
Si <sup>7+</sup>	14	0.07216	0.31274	0.36271	300.0883	303.54	0.0114
P <sup>8+</sup>	15	0.06730	0.29010	0.33191	368.9298	372.13	0.0086
S <sup>9+</sup>	16	0.06306	0.27053	0.30595	444.7137	447.5	0.0062
Cl <sup>10+</sup>	17	0.05932	0.25344	0.28376	527.4312	529.28	0.0035
Ar <sup>11+</sup>	18	0.05599	0.23839	0.26459	617.0761	618.26	0.0019
K <sup>12+</sup>	19	0.05302	0.22503	0.24785	713.6436	714.6	0.0013
Ca <sup>13+</sup>	20	0.05035	0.21308	0.23311	817.1303	817.6	0.0006
Sc <sup>14+</sup>	21	0.04794	0.20235	0.22003	927.5333	927.5	0.0000
Ti <sup>15+</sup>	22	0.04574	0.19264	0.20835	1044.8504	1044	-0.0008
V <sup>16+</sup>	23	0.04374	0.18383	0.19785	1169.0800	1168	-0.0009
Cr <sup>17+</sup>	24	0.04191	0.17579	0.18836	1300.2206	1299	-0.0009
Mn <sup>18+</sup>	25	0.04022	0.16842	0.17974	1438.2710	1437	-0.0009
Fe <sup>19+</sup>	26	0.03867	0.16165	0.17187	1583.2303	1582	-0.0008
Co <sup>20+</sup>	27	0.03723	0.15540	0.16467	1735.0978	1735	-0.0001
Ni <sup>21+</sup>	28	0.03589	0.14961	0.15805	1893.8726	1894	0.0001
Cu <sup>22+</sup>	29	0.03465	0.14424	0.15194	2059.5543	2060	0.0002

<sup>a</sup> Radius of the first set of paired inner electrons of seven-electron atoms from Eq. (10.51).<sup>b</sup> Radius of the second set of paired inner electrons of seven-electron atoms from Eq. (10.62).<sup>c</sup> Radius of the three unpaired paired outer electrons of seven-electron atoms from Eq. (10.152) for  $Z > 7$  and Eq. (10.142) for  $N$ .<sup>d</sup> Calculated ionization energies of seven-electron atoms given by the electric energy (Eq. (10.153)).<sup>e</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.5 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The nitrogen atom isoelectronic series is given in Table 10.5 [2-3] to much higher

precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of N isoelectronic and Rydberg series, as well as direct experimental data.

### EIGHT-ELECTRON ATOMS

Eight-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, and seven-electron atoms.

### RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE OXYGEN ATOM

For each seven-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62), and three unpaired electrons in an orbitsphere at  $r_7$  given by Eq. (10.152). For  $Z \geq 8$ , the next electron which binds to form the corresponding eight-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-pairing force that results in the formation of a filled  $s$  orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (10.71) with the radius  $r_8$ ) reduces the energy of the atom less than that due to the alternative forces on two paired electrons in a  $p_x$  orbital and two unpaired electrons in  $p_y$  and  $p_z$  orbitals of an orbitsphere at the same radius  $r_8$ . The resulting electron configuration is  $1s^2 2s^2 2p^4$ , and the orbital arrangement is

$$\begin{array}{ccc} \uparrow \downarrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array} \quad (10.154)$$

corresponding to the ground state  $^3P_2$ .

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner seven electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$F_{ele} = \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} \mathbf{i}_r \quad (10.155)$$

for  $r > r_7$ .

The energy is minimized with conservation of angular momentum by the cancellation of the orbital angular momentum of a  $p_x$  electron by that of the  $p_y$  electron with the pairing of electron eight to fill the  $p_x$  orbital. Then, the diamagnetic force is that of  $N$  given by Eq. (10.136) corresponding to the  $p_z$ -orbital electron (Eq. (10.82) with  $m=0$ ) as the source of diamagnetism with an additional contribution from the uncanceled  $p_x$  electron (Eq. (10.82) with  $m=1$ ).  $F_{\text{diamagnetic}}$  for the oxygen atom is

$$F_{\text{diamagnetic}} = -\left(\frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_8^2 r_3} \sqrt{s(s+1)} \hat{i}_r = -\frac{\hbar^2}{4m_e r_8^2 r_3} \sqrt{s(s+1)} \hat{i}_r \quad (10.156)$$

From Eqs. (10.83) and (10.89),  $F_{\text{mag}2}$  is

$$F_{\text{mag}2} = (1+1) \frac{1}{Z} \frac{\hbar^2}{m_e r_8^2 r_3} \sqrt{s(s+1)} \hat{i}_r = \frac{1}{Z} \frac{2\hbar^2}{m_e r_8^2 r_3} \sqrt{s(s+1)} \hat{i}_r \quad (10.157)$$

corresponding to the spin-angular-momentum contribution alone of the  $p_x$  electron and the orbital angular momentum of the  $p_z$  electron, respectively.

The outward centrifugal force on electron 8 is balanced by the electric force and the magnetic forces (on electron 8). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.155)), diamagnetic (Eq. (10.156)), and paramagnetic (Eq. (10.157)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} - \frac{\hbar^2}{4m_e r_8^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_8^2 r_3} \sqrt{s(s+1)} \quad (10.158)$$

Substitution of  $v_8 = \frac{\hbar}{m_e r_8}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.158) gives:

$$\frac{\hbar^2}{m_e r_8^3} = \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} - \frac{\hbar^2}{4m_e r_8^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_8^2 r_3} \sqrt{\frac{3}{4}} \quad (10.159)$$

$$r_8 = \frac{\frac{\hbar^2}{m_e}}{\frac{(Z-7)e^2}{4\pi\epsilon_0} - \frac{\hbar^2}{4m_e r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_3} \sqrt{\frac{3}{4}}} \quad (10.160)$$

$$r_8 = \frac{a_0}{(Z-7) - \left(\frac{1}{4} - \frac{2}{Z}\right) \sqrt{\frac{3}{4}}}, \quad r_3 \text{ in units of } a_0 \quad (10.161)$$

Substitution of  $\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with  $Z=8$ ) into Eq. (10.161) gives

$$r_8 = a_0 \quad (10.162)$$

The ionization energy of the oxygen atom is given by the negative



of  $E(\text{electric})$  given by Eq. (10.102) with the appropriate charge and radius:

$$E(\text{ionization}; O) = -\text{Electric Energy} = \frac{(Z-7)e^2}{8\pi\epsilon_0 r_8} = 13.60580 \text{ eV} \quad (10.163)$$

where  $r_8 = a_0$  (Eq. (10.162)) and  $Z=8$ . The experimental ionization energy of the oxygen atom is 13.6181 eV [3].

### THE IONIZATION ENERGIES OF EIGHT-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z>8$

Eight-electron atoms having  $Z>8$  possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that  $F_{\text{diamagnetic}}$  is minimized while  $F_{\text{mag}2}$  is maximized. From Eq. (10.82), the diamagnetic force,  $F_{\text{diamagnetic}}$ , is given by the sum of the contributions from the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals corresponding to  $m = 1, -1$ , and  $0$ , respectively:

$$F_{\text{diamagnetic}} = -\left(\frac{2}{3} + \frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_8^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_8^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.164)$$

The filled p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is only due to the electrons at  $r_3$ . From Eqs. (10.84) and (10.89),  $F_{\text{mag}2}$  is

$$F_{\text{mag}2} = (4+1+1) \frac{1}{Z} \frac{\hbar^2}{m_e r_8^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{6\hbar^2}{m_e r_8^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.165)$$

corresponding to the spin and orbital angular momenta of the paired  $p_x$  electrons and the orbital angular momentum of each of the  $p_y$  and  $p_z$  electrons, respectively.

The second diamagnetic force,  $F_{\text{diamagnetic}2}$ , due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$F_{\text{diamagnetic}2} = -\left[\frac{Z-8}{Z-7}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_8^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (10.166)$$

In the case that  $Z>8$ , the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.155)), diamagnetic (Eqs. (10.164) and (10.166)), and paramagnetic (Eq. (10.165)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} - \frac{5\hbar^2}{12m_e r_8^2 r_3} \sqrt{s(s+1)} + \frac{6\hbar^2}{Zm_e r_8^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-8}{Z-7}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_8^4} 10 \sqrt{s(s+1)} \quad (10.167)$$

Substitution of  $v_8 = \frac{\hbar}{m_e r_8}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.167) gives:

$$\frac{\hbar^2}{m_e r_8^3} = \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} - \frac{5\hbar^2}{12 m_e r_8^2 r_3} \sqrt{\frac{3}{4}} + \frac{6\hbar^2}{Z m_e r_8^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_8^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (10.168)$$

The quadratic equation corresponding to Eq. (10.168) is

$$\left( \frac{(Z-7)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) r_8^2 - \frac{\hbar^2}{m_e} r_8 - \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{m_e} 10 \sqrt{\frac{3}{4}} = 0 \quad (10.169)$$

$$r_8^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-7)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_8 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-7)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (10.170)$$

The solution of Eq. (10.170) using the quadratic formula is:

$$r_8 = \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-7)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} \pm \frac{\sqrt{\left( \frac{\hbar^2}{m_e} \right)^2 + 4 \left( \frac{(Z-7)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{6}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) \frac{\hbar^2}{m_e} \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}}{2} \quad (10.171)$$

$$r_8 = \frac{a_0}{\left( (Z-7) - \left( \frac{5}{24} - \frac{3}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \pm a_0 \frac{\sqrt{\left( \frac{1}{\left( (Z-7) - \left( \frac{5}{24} - \frac{3}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \right)^2 + 20\sqrt{3} \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}}{\left( (Z-7) - \left( \frac{5}{24} - \frac{3}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \quad (10.172)$$

$r_3$  in units of  $a_0$

where  $r_3$  is given by Eq. (10.62). The positive root of Eq. (10.172) must

be taken in order that  $r_8 > 0$ . The final radius of electron 8,  $r_8$ , is given by Eq. (10.172); this is also the final radius of electrons 5, 6, and 7. The radii of several eight-electron atoms are given in Table 10.6.

The ionization energies for the eight-electron atoms with  $Z > 8$  are given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radii,  $r_8$ , given by Eq. (10.172)):

$$E(\text{Ionization}) = -\text{Electric Energy} = \frac{(Z-7)e^2}{8\pi\epsilon_0 r_8} \quad (10.173)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured eight-electron atoms are given in Table 10.6.

Table 10.6. Ionization energies for some eight-electron atoms.

8 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_3$ ( $a_0$ ) <sup>b</sup>	$r_8$ ( $a_0$ ) <sup>c</sup>	Theoretical Ionization Energies <sup>d</sup> (eV)	Experimental Ionization Energies <sup>e</sup> (eV)	Relative Error
O	8	0.12739	0.59020	1.00000	13.60580	13.6181	0.0009
F <sup>+</sup>	9	0.11297	0.51382	0.7649	35.5773	34.9708	-0.0173
Ne <sup>2+</sup>	10	0.10149	0.45511	0.6514	62.6611	63.45	0.0124
Na <sup>3+</sup>	11	0.09213	0.40853	0.5592	97.3147	98.91	0.0161
Mg <sup>4+</sup>	12	0.08435	0.37065	0.4887	139.1911	141.27	0.0147
Al <sup>5+</sup>	13	0.07778	0.33923	0.4338	188.1652	190.49	0.0122
Si <sup>6+</sup>	14	0.07216	0.31274	0.3901	244.1735	246.5	0.0094
P <sup>7+</sup>	15	0.06730	0.29010	0.3543	307.1791	309.6	0.0078
S <sup>8+</sup>	16	0.06306	0.27053	0.3247	377.1579	379.55	0.0063
Cl <sup>9+</sup>	17	0.05932	0.25344	0.2996	454.0940	455.63	0.0034
Ar <sup>10+</sup>	18	0.05599	0.23839	0.2782	537.9756	538.96	0.0018
K <sup>11+</sup>	19	0.05302	0.22503	0.2597	628.7944	629.4	0.0010
Ca <sup>12+</sup>	20	0.05035	0.21308	0.2434	726.5442	726.6	0.0001
Sc <sup>13+</sup>	21	0.04794	0.20235	0.2292	831.2199	830.8	-0.0005
Ti <sup>14+</sup>	22	0.04574	0.19264	0.2165	942.8179	941.9	-0.0010
V <sup>15+</sup>	23	0.04374	0.18383	0.2051	1061.3351	1060	-0.0013
Cr <sup>16+</sup>	24	0.04191	0.17579	0.1949	1186.7691	1185	-0.0015
Mn <sup>17+</sup>	25	0.04022	0.16842	0.1857	1319.1179	1317	-0.0016
Fe <sup>18+</sup>	26	0.03867	0.16165	0.1773	1458.3799	1456	-0.0016
Co <sup>19+</sup>	27	0.03723	0.15540	0.1696	1604.5538	1603	-0.0010
Ni <sup>20+</sup>	28	0.03589	0.14961	0.1626	1757.6383	1756	-0.0009
Cu <sup>21+</sup>	29	0.03465	0.14424	0.1561	1917.6326	1916	-0.0009

<sup>a</sup> Radius of the first set of paired inner electrons of eight-electron atoms from Eq. (10.51).

<sup>b</sup> Radius of the second set of paired inner electrons of eight-electron atoms from Eq. (10.62).

<sup>c</sup> Radius of the two paired and two unpaired outer electrons of eight-electron atoms from Eq.

(10.172) for  $Z > 8$  and Eq. (10.162) for  $O$ .

<sup>d</sup> Calculated ionization energies of eight-electron atoms given by the electric energy (Eq. (10.173)).

<sup>e</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.6 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The oxygen atom isoelectronic series is given in Table 10.6 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of O isoelectronic and Rydberg series, as well as direct experimental data.

#### NINE-ELECTRON ATOMS

Nine-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, and eight-electron atoms.

#### RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE FLUORINE ATOM

For each eight-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62), and two paired and unpaired electrons in an orbitsphere at  $r_5$  given by Eq. (10.172). For  $Z \geq 9$ , the next electron which binds to form the corresponding nine-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-pairing force that results in the formation of a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (10.71) with the radius  $r_5$ ) reduces the energy of the atom less than that due to the alternative forces on an unpaired electron in a  $p_y$  orbital and two pairs of electrons of opposite spin in  $p_x$  and  $p_z$  orbitals of an orbitsphere at the same radius  $r_5$ . The resulting electron

configuration is  $1s^2 2s^2 2p^5$ , and the orbital arrangement is

$$\begin{array}{ccc} \uparrow \downarrow & \uparrow \downarrow & \uparrow \\ 1 & 0 & -1 \end{array} \quad (10.174)$$

corresponding to the ground state  $^2P_{3/2}^0$ .

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner eight electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-8)e^2}{4\pi\epsilon_0 r_9^2} \mathbf{i}_r \quad (10.175)$$

for  $r > r_8$ .

The energy is minimized and the angular momentum is conserved with the pairing of electron nine to fill the  $p_z$  orbital when the orbital angular momenta of each set of  $p_x$  and  $p_z$  spin-paired electrons adds negatively to cancel. Then, the diamagnetic force (Eq. (10.82)),  $\mathbf{F}_{diamagnetic}$ , is

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_9^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.176)$$

corresponding to  $m = -1$  for the unpaired  $p_y$  electron.

From Eqs. (10.83) and (10.89),  $\mathbf{F}_{mag2}$  is

$$\mathbf{F}_{mag2} = (1+1+1) \frac{1}{Z} \frac{\hbar^2}{m_e r_9^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{3\hbar^2}{m_e r_9^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.177)$$

corresponding to the spin-angular-momentum contribution alone from each of the  $p_x$  and  $p_z$  orbitals and the orbital-angular-momentum contribution of the  $p_y$  electron, respectively.

The outward centrifugal force on electron 9 is balanced by the electric force and the magnetic forces (on electron 9). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.175)), diamagnetic (Eq. (10.176)), and paramagnetic (Eq. (10.177)) forces as follows:

$$\frac{m_e v_9^2}{r_9} = \frac{(Z-8)e^2}{4\pi\epsilon_0 r_9^2} - \frac{\hbar^2}{6m_e r_9^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_9^2 r_3} \sqrt{s(s+1)} \quad (10.178)$$

Substitution of  $v_9 = \frac{\hbar}{m_e r_9}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.178) gives:

$$\frac{\hbar^2}{m_e r_9^3} = \frac{(Z-8)e^2}{4\pi\epsilon_0 r_9^2} - \frac{\hbar^2}{6m_e r_9^2 r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_9^2 r_3} \sqrt{\frac{3}{4}} \quad (10.179)$$

$$r_9 = \frac{\frac{\hbar^2}{m_e}}{\frac{(Z-8)e^2}{4\pi\epsilon_0} - \frac{\hbar^2}{6m_e r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_3} \sqrt{\frac{3}{4}}} \quad (10.180)$$

$$r_9 = \frac{a_0}{(Z-8) - \left(\frac{1}{6} - \frac{3}{Z}\right) \sqrt{\frac{3}{4}} \frac{1}{r_3}}, \quad r_3 \text{ in units of } a_0 \quad (10.181)$$

Substitution of  $\frac{r_1}{a_0} = 0.51382$  (Eq. (10.62) with  $Z=9$ ) into Eq. (10.181)

gives

$$r_9 = 0.78069a_0 \quad (10.182)$$

The ionization energy of the fluorine atom is given by the negative of  $E(\text{electric})$  given by Eq. (10.102) with the appropriate charge and radius:

$$E(\text{ionization}; F) = -\text{Electric Energy} = \frac{(Z-8)e^2}{8\pi\epsilon_0 r_9} = 17.42782 \text{ eV} \quad (10.183)$$

where  $r_9 = 0.78069a_0$  (Eq. (10.183)) and  $Z=9$ . The experimental ionization energy of the fluorine atom is 17.42282 eV [3].

### THE IONIZATION ENERGIES OF NINE-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z>9$

Nine-electron atoms having  $Z>9$  possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that  $F_{\text{diamagnetic}}$  is minimized while  $F_{\text{mag}2}$  is maximized. From Eq. (10.82), the diamagnetic force,  $F_{\text{diamagnetic}}$ , is given by the sum of the contributions from the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals corresponding to  $m = 1, -1$ , and  $0$ , respectively:

$$F_{\text{diamagnetic}} = -\left(\frac{2}{3} + \frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_9^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_9^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.184)$$

The filled p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is only due to the electrons at  $r_3$ . From Eqs. (10.84) and (10.89),  $F_{\text{mag}2}$  is

$$F_{\text{mag}2} = (4+4+1) \frac{1}{Z} \frac{\hbar^2}{m_e r_9^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{9\hbar^2}{m_e r_9^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.185)$$

corresponding to the spin and orbital angular momenta of the paired  $p_x$  and  $p_z$  electrons and the orbital angular momentum of the unpaired  $p_y$  electron, respectively.

The second diamagnetic force,  $F_{\text{diamagnetic2}}$ , due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$F_{\text{diamagnetic2}} = -\left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_9^4} 10\sqrt{s(s+1)}\hat{i}, \quad (10.186)$$

In the case that  $Z > 9$ , the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.175)), diamagnetic (Eqs. (10.184) and (10.186)), and paramagnetic (Eq. (10.185)) forces as follows:

$$\frac{m_e v_9^2}{r_9} = \frac{(Z-8)e^2}{4\pi\epsilon_0 r_9^2} - \frac{5\hbar^2}{12m_e r_9^2 r_3} \sqrt{s(s+1)} + \frac{9\hbar^2}{Zm_e r_9^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_9^4} 10\sqrt{s(s+1)} \quad (10.187)$$

Substitution of  $v_9 = \frac{\hbar}{m_e r_9}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.187) gives:

$$\frac{\hbar^2}{m_e r_9^3} = \frac{(Z-8)e^2}{4\pi\epsilon_0 r_9^2} - \frac{5\hbar^2}{12m_e r_9^2 r_3} \sqrt{\frac{3}{4}} + \frac{9\hbar^2}{Zm_e r_9^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_9^4} 10\sqrt{\frac{3}{4}} \quad (10.188)$$

The quadratic equation corresponding to Eq. (10.188) is

$$\left(\frac{(Z-8)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{9}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)r_9^2 - \frac{\hbar^2}{m_e} r_9 - \left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e} 10\sqrt{\frac{3}{4}} = 0 \quad (10.189)$$

$$r_9^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-8)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{9}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} r_9 - \frac{\frac{\hbar^2}{m_e} \left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-8)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{9}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} = 0 \quad (10.190)$$

The solution of Eq. (10.190) using the quadratic formula is:

$$r_9 = \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-8)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{9}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} \pm \sqrt{\left(\frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-8)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{9}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)}\right)^2 + 4\frac{\frac{\hbar^2}{m_e} \left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-8)e^2}{4\pi\epsilon_0} - \left(\frac{5}{12} - \frac{9}{Z}\right)\frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)}} \quad (10.191)$$

$$r_9 = \frac{\left( (Z-8) - \left( \frac{5}{24} - \frac{9}{2Z} \right) \frac{\sqrt{3}}{r_3} \right) \pm a_0 \sqrt{\frac{1}{\left( (Z-8) - \left( \frac{5}{24} - \frac{9}{2Z} \right) \frac{\sqrt{3}}{r_3} \right)^2} + \frac{20\sqrt{3} \left( \left[ \frac{Z-9}{Z-8} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}{\left( (Z-8) - \left( \frac{5}{24} - \frac{9}{2Z} \right) \frac{\sqrt{3}}{r_3} \right)}}}{2} \quad (10.192)$$

$r_3$  in units of  $a_0$

where  $r_3$  is given by Eq. (10.62). The positive root of Eq. (10.192) must be taken in order that  $r_9 > 0$ . The final radius of electron 9,  $r_9$ , is given by Eq. (10.192); this is also the final radius of electrons 5, 6, 7, and 8. The radii of several nine-electron atoms are given in Table 10.7.

The ionization energies for the nine-electron atoms with  $Z > 9$  are given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radii,  $r_9$ , given by Eq. (10.192)):

$$E(\text{Ionization}) = - \text{Electric Energy} = \frac{(Z-8)e^2}{8\pi\epsilon_0 r_9} \quad (10.193)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured nine-electron atoms are given in Table 10.7.



Table 10.7. Ionization energies for some nine-electron atoms.

9 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_3$ ( $a_0$ ) <sup>b</sup>	$r_9$ ( $a_0$ ) <sup>c</sup>	Theoretical Ionization Energies <sup>d</sup> (eV)	Experimental Ionization Energies <sup>e</sup> (eV)	Relative Error
F	9	0.11297	0.51382	0.78069	17.42782	17.42282	-0.0003
Ne <sup>+</sup>	10	0.10149	0.45511	0.64771	42.0121	40.96328	-0.0256
Na <sup>2+</sup>	11	0.09213	0.40853	0.57282	71.2573	71.62	0.0051
Mg <sup>3+</sup>	12	0.08435	0.37065	0.50274	108.2522	109.2655	0.0093
Al <sup>4+</sup>	13	0.07778	0.33923	0.44595	152.5469	153.825	0.0083
Si <sup>5+</sup>	14	0.07216	0.31274	0.40020	203.9865	205.27	0.0063
P <sup>6+</sup>	15	0.06730	0.29010	0.36283	262.4940	263.57	0.0041
S <sup>7+</sup>	16	0.06306	0.27053	0.33182	328.0238	328.75	0.0022
Cl <sup>8+</sup>	17	0.05932	0.25344	0.30571	400.5466	400.06	-0.0012
Ar <sup>9+</sup>	18	0.05599	0.23839	0.28343	480.0424	478.69	-0.0028
K <sup>10+</sup>	19	0.05302	0.22503	0.26419	566.4968	564.7	-0.0032
Ca <sup>11+</sup>	20	0.05035	0.21308	0.24742	659.8992	657.2	-0.0041
Sc <sup>12+</sup>	21	0.04794	0.20235	0.23266	760.2415	756.7	-0.0047
Ti <sup>13+</sup>	22	0.04574	0.19264	0.21957	867.5176	863.1	-0.0051
V <sup>14+</sup>	23	0.04374	0.18383	0.20789	981.7224	976	-0.0059
Cr <sup>15+</sup>	24	0.04191	0.17579	0.19739	1102.8523	1097	-0.0053
Mn <sup>16+</sup>	25	0.04022	0.16842	0.18791	1230.9038	1224	-0.0056
Fe <sup>17+</sup>	26	0.03867	0.16165	0.17930	1365.8746	1358	-0.0058
Co <sup>18+</sup>	27	0.03723	0.15540	0.17145	1507.7624	1504.6	-0.0021
Ni <sup>19+</sup>	28	0.03589	0.14961	0.16427	1656.5654	1648	-0.0052
Cu <sup>20+</sup>	29	0.03465	0.14424	0.15766	1812.2821	1804	-0.0046

<sup>a</sup> Radius of the first set of paired inner electrons of nine-electron atoms from Equation (10.51).

<sup>b</sup> Radius of the second set of paired inner electrons of nine-electron atoms from Equation (10.62).

<sup>c</sup> Radius of the one unpaired and two sets of paired outer electrons of nine-electron atoms from Eq. (10.192) for  $Z > 9$  and Eq. (10.182) for  $F$ .

<sup>d</sup> Calculated ionization energies of nine-electron atoms given by the electric energy (Eq. (10.193)).

<sup>e</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.7 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The fluorine atom isoelectronic series is given in Table 10.7 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are

based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of F isoelectronic and Rydberg series, as well as direct experimental data.

### TEN-ELECTRON ATOMS

Ten-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, and nine-electron atoms.

### RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE NEON ATOM

For each nine-electron atom having a central charge of  $Z$  times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62), and two sets of paired and an unpaired electron is in an orbitsphere at  $r_5$  given by Eq. (10.192). For  $Z \geq 10$ , the next electron which binds to form the corresponding ten-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-pairing force that results in the formation of a filled  $s$  orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (10.71) with the radius  $r_{10}$ ) reduces the energy of the atom less than that due to the alternative forces on three pairs of electrons of opposite spin in  $p_x$ ,  $p_y$ , and  $p_z$  orbitals of an orbitsphere at the same radius  $r_{10}$ . The resulting electron configuration is  $1s^2 2s^2 2p^6$ , and the orbital arrangement is

$$\begin{array}{ccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ 1 & 0 & -1 \end{array} \quad (10.194)$$

corresponding to the ground state  $^1S_0$ .

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner nine electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$F_{ele} = \frac{(Z-9)e^2}{4\pi\epsilon_0 r_{10}^2} \mathbf{i}_r \quad (10.195)$$

for  $r > r_5$ .

The energy is minimized and the angular momentum is conserved with the pairing of electron ten to fill the  $p_y$  orbital when the orbital angular momenta of each set of the  $p_x$ ,  $p_y$ , and  $p_z$  spin-paired electrons adds negatively to cancel. Then, the diamagnetic force (Eq. (10.82)),  $F_{\text{diamagnetic}}$ , is zero:

$$F_{\text{diamagnetic}} = 0 \quad (10.196)$$

From Eq. (10.83),  $F_{\text{mag}2}$  is

$$F_{\text{mag}2} = (1+1+1) \frac{1}{Z} \frac{\hbar^2}{m_e r_{10}^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{3\hbar^2}{m_e r_{10}^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.197)$$

corresponding to the spin-angular-momentum contribution alone from each of the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals.

The outward centrifugal force on electron 10 is balanced by the electric force and the magnetic forces (on electron 10). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.195)), diamagnetic (Eq. (10.196)), and paramagnetic (Eq. (10.197)) forces as follows:

$$\frac{m_e v_{10}^2}{r_{10}} = \frac{(Z-9)e^2}{4\pi\epsilon_0 r_{10}^2} + \frac{3\hbar^2}{Z m_e r_{10}^2 r_3} \sqrt{s(s+1)} \quad (10.198)$$

Substitution of  $v_{10} = \frac{\hbar}{m_e r_{10}}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.198) gives:

$$\frac{\hbar^2}{m_e r_{10}^3} = \frac{(Z-9)e^2}{4\pi\epsilon_0 r_{10}^2} + \frac{3\hbar^2}{Z m_e r_{10}^2 r_3} \sqrt{\frac{3}{4}} \quad (10.199)$$

$$r_{10} = \frac{\frac{\hbar^2}{m_e}}{\frac{(Z-9)e^2}{4\pi\epsilon_0} + \frac{3\hbar^2}{Z m_e r_3} \sqrt{\frac{3}{4}}} \quad (10.200)$$

$$r_{10} = \frac{a_0}{(Z-9) + \frac{3}{Z} \frac{\sqrt{\frac{3}{4}}}{r_3}}, \quad r_3 \text{ in units of } a_0 \quad (10.201)$$

Substitution of  $\frac{r_1}{a_0} = 0.45511$  (Eq. (10.62) with  $Z=10$ ) into Eq. (10.201)

gives

$$r_{10} = 0.63659 a_0 \quad (10.202)$$

The ionization energy of the neon atom is given by the negative of  $E(\text{electric})$  given by Eq. (10.102) with the appropriate charge and radius:

$$E(\text{ionization}; \text{Ne}) = -\text{Electric Energy} = \frac{(Z-9)e^2}{8\pi\epsilon_0 r_{10}} = 21.37296 \text{ eV} \quad (10.203)$$

where  $r_{10} = 0.63659 a_0$  (Eq. (10.202)) and  $Z=10$ . The experimental

ionization energy of the neon atom is 21.56454 eV [3].

### THE IONIZATION ENERGIES OF TEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE $Z > 10$

Ten-electron atoms having  $Z > 10$  possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that  $F_{\text{diamagnetic}}$  is minimized while  $F_{\text{mag}2}$  is maximized. From Eq. (10.82), the diamagnetic force,  $F_{\text{diamagnetic}}$ , is given by the sum of the contributions from the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals corresponding to  $m = 1, -1$ , and 0, respectively:

$$F_{\text{diamagnetic}} = -\left(\frac{2}{3} + \frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_{10}^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_{10}^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.204)$$

The filled p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is only due to the electrons at  $r_3$ . From Eq. (10.84),  $F_{\text{mag}2}$  is

$$F_{\text{mag}2} = (4 + 4 + 4) \frac{1}{Z} \frac{\hbar^2}{m_e r_{10}^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = \frac{12\hbar^2}{Z m_e r_{10}^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (10.205)$$

corresponding to the spin and orbital angular momenta of the paired  $p_x$ ,  $p_y$ , and  $p_z$  electrons.

The second diamagnetic force,  $F_{\text{diamagnetic}2}$ , due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$F_{\text{diamagnetic}2} = -\left[\frac{Z-10}{Z-9}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_{10}^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (10.206)$$

In the case that  $Z > 10$ , the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.195)), diamagnetic (Eqs. (10.204) and (10.206)), and paramagnetic (Eq. (10.205)) forces as follows:

$$\frac{m_e v_{10}^2}{r_{10}} = \frac{(Z-9)e^2}{4\pi\epsilon_0 r_{10}^2} - \frac{5\hbar^2}{12m_e r_{10}^2 r_3} \sqrt{s(s+1)} + \frac{12\hbar^2}{Zm_e r_{10}^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-10}{Z-9}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_{10}^4} 10 \sqrt{s(s+1)} \quad (10.207)$$

Substitution of  $v_{10} = \frac{\hbar}{m_e r_{10}}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (10.207) gives:

$$\frac{\hbar^2}{m_e r_{10}^3} = \frac{(Z-9)e^2}{4\pi\epsilon_0 r_{10}^2} - \frac{5\hbar^2}{12m_e r_{10}^2 r_3} \sqrt{\frac{3}{4}} + \frac{12\hbar^2}{Zm_e r_{10}^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-10}{Z-9}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_{10}^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (10.208)$$

The quadratic equation corresponding to Eq. (10.208) is

$$\left( \frac{(Z-9)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{12}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) r_{10}^2 - \frac{\hbar^2}{m_e} r_{10} - \left[ \frac{Z-10}{Z-9} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{m_e} 10 \sqrt{\frac{3}{4}} = 0 \quad (10.209)$$

$$r_{10}^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-9)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{12}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_{10} - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-10}{Z-9} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-9)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{12}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (10.210)$$

The solution of Eq. (10.210) using the quadratic formula is:

$$r_{10} = \frac{\frac{\hbar^2}{m_e} \left( \frac{(Z-9)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{12}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) \pm \sqrt{\left( \frac{\hbar^2}{m_e} \left( \frac{(Z-9)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{12}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right) \right)^2 + 4 \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-10}{Z-9} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-9)e^2}{4\pi\epsilon_0} - \left( \frac{5}{12} - \frac{12}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)}}}{2} \quad (10.211)$$

$$r_{10} = \frac{\frac{a_0}{\left( (Z-9) - \left( \frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \pm a_0 \sqrt{\left( \frac{1}{\left( (Z-9) - \left( \frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \right)^2 + \frac{20\sqrt{3} \left[ \frac{Z-10}{Z-9} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-9) - \left( \frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)}}}{2} \quad (10.212)$$

$r_3$  in units of  $a_0$

where  $r_3$  is given by Eq. (10.62). The positive root of Eq. (10.212) must be taken in order that  $r_{10} > 0$ . The final radius of electron 10,  $r_{10}$ , is given by Eq. (10.62); this is also the final radius of electrons 5, 6, 7, 8, and 9. The radii of several ten-electron atoms are given in Table 10.8.

The ionization energies for the ten-electron atoms with  $Z > 10$  are given by the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radii,  $r_{10}$ , given by Eq. (10.212)):

$$E(\text{Ionization}) = -\text{Electric Energy} = \frac{(Z-9)e^2}{8\pi\epsilon_0 r_{10}} \quad (10.213)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured ten-electron atoms are given in Table 10.8.

Table 10.8. Ionization energies for some ten-electron atoms.

10 e Atom	Z	$r_1$ ( $a_0$ ) <sup>a</sup>	$r_3$ ( $a_0$ ) <sup>b</sup>	$r_{10}$ ( $a_0$ ) <sup>c</sup>	Theoretical Ionization Energies <sup>d</sup> (eV)	Experimental Ionization Energies <sup>e</sup> (eV)	Relative Error
Ne	10	0.10149	0.45511	0.63659	21.37296	21.56454	0.00888
Na <sup>+</sup>	11	0.09213	0.40853	0.560945	48.5103	47.2864	-0.0259
Mg <sup>2+</sup>	12	0.08435	0.37065	0.510568	79.9451	80.1437	0.0025
Al <sup>3+</sup>	13	0.07778	0.33923	0.456203	119.2960	119.992	0.0058
Si <sup>4+</sup>	14	0.07216	0.31274	0.409776	166.0150	166.767	0.0045
P <sup>5+</sup>	15	0.06730	0.29010	0.371201	219.9211	220.421	0.0023
S <sup>6+</sup>	16	0.06306	0.27053	0.339025	280.9252	280.948	0.0001
Cl <sup>7+</sup>	17	0.05932	0.25344	0.311903	348.9750	348.28	-0.0020
Ar <sup>8+</sup>	18	0.05599	0.23839	0.288778	424.0365	422.45	-0.0038
K <sup>9+</sup>	19	0.05302	0.22503	0.268844	506.0861	503.8	-0.0045
Ca <sup>10+</sup>	20	0.05035	0.21308	0.251491	595.1070	591.9	-0.0054
Sc <sup>11+</sup>	21	0.04794	0.20235	0.236251	691.0866	687.36	-0.0054
Ti <sup>12+</sup>	22	0.04574	0.19264	0.222761	794.0151	787.84	-0.0078
V <sup>13+</sup>	23	0.04374	0.18383	0.210736	903.8853	896	-0.0088
Cr <sup>14+</sup>	24	0.04191	0.17579	0.19995	1020.6910	1010.6	-0.0100
Mn <sup>15+</sup>	25	0.04022	0.16842	0.19022	1144.4276	1134.7	-0.0086
Fe <sup>16+</sup>	26	0.03867	0.16165	0.181398	1275.0911	1266	-0.0072
Co <sup>17+</sup>	27	0.03723	0.15540	0.173362	1412.6783	1397.2	-0.0111
Ni <sup>18+</sup>	28	0.03589	0.14961	0.166011	1557.1867	1541	-0.0105
Cu <sup>19+</sup>	29	0.03465	0.14424	0.159261	1708.6139	1697	-0.0068
Zn <sup>20+</sup>	30	0.03349	0.13925	0.153041	1866.9581	1856	-0.0059

<sup>a</sup> Radius of the first set of paired inner electrons of ten-electron atoms from Equation (10.51).

<sup>b</sup> Radius of the second set of paired inner electrons of ten-electron atoms from Equation (10.62).

<sup>c</sup> Radius of three sets of paired outer electrons of ten-electron atoms from Eq. (10.212) for  $Z > 10$  and Eq. (10.202) for  $Ne$ .

<sup>d</sup> Calculated ionization energies of ten-electron atoms given by the electric energy (Eq. (10.213)).

<sup>e</sup> From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

The agreement between the experimental and calculated values of Table 10.8 is well within the experimental capability of the spectroscopic determinations including the values at large  $Z$  which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The neon atom isoelectronic series is given in Table 10.8 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are

based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Ne isoelectronic and Rydberg series, as well as direct experimental data.

#### GENERAL EQUATION FOR THE IONIZATION ENERGIES OF FIVE THROUGH TEN-ELECTRON ATOMS

Using the forces given by Eqs. (10.70), (10.82-10.84), (10.89), (10.93), and the radii  $r_3$  given by Eq. (10.62), the radii of the 2p electrons of all five through ten-electron atoms may be solved exactly. The electric energy given by Eq. (10.102) gives the corresponding exact ionization energies. A summary of the parameters of the equations that determine the exact radii and ionization energies of all five through ten-electron atoms is given in Table 10.9.

$F_{ele}$  and  $F_{diamagnetic2}$  given by Eqs. (10.70) and (10.93), respectively, are of the same form for all atoms with the appropriate nuclear charges and atomic radii.  $F_{diamagnetic}$  given by Eq. (10.82) and  $F_{mag2}$  given by Eqs. (10.83-10.84) and (10.89) are of the same form with the appropriate factors that depend on the electron configuration wherein the electron configuration must be a minimum of energy.

For each n-electron atom having a central charge of  $Z$  times that of the proton and an electron configuration  $1s^2 2s^2 2p^{n-4}$ , there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by Eq. (7.19) and (10.51):

$$r_1 = r_2 = a_0 \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right] \quad (10.214)$$

two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by Eq. (10.62):



$$r_4 = r_3 = \frac{a_0 \left( 1 - \frac{\sqrt{3}}{4} \frac{1}{Z} \right) \pm a_0 \sqrt{\left( 1 - \frac{\sqrt{3}}{4} \frac{1}{Z} \right)^2 + 4 \left( \frac{[Z-3]}{[Z-2]} r_1^{10} \sqrt{\frac{3}{4}} \right)}}{\left( (Z-3) - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{3}}{r_1} \right) \pm \left( (Z-3) - \left( \frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{3}}{r_1} \right)} \quad (10.215)$$

 $r_1$  in units of  $a_0$ 

where  $r_1$  is given by Eq. (10.214), and  $n-4$  electrons in an orbitsphere with radius  $r_n$  given by

$$r_n = \frac{a_0 \left( (Z-(n-1)) - \left( \frac{A}{8} - \frac{B}{2Z} \right) \frac{\sqrt{3}}{r_3} \right) \pm a_0 \sqrt{\left( (Z-(n-1)) - \left( \frac{A}{8} - \frac{B}{2Z} \right) \frac{\sqrt{3}}{r_3} \right)^2 + 20\sqrt{3} \left( \left[ \frac{Z-n}{Z-(n-1)} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}}{2} \quad (10.216)$$

 $r_3$  in units of  $a_0$ 

where  $r_3$  is given by Eq. (10.215), the parameter  $A$  given in Table 10.9 corresponds to the diamagnetic force,  $F_{\text{diamagnetic}}$  (Eq. (10.82)), and the parameter  $B$  given in Table 10.9 corresponds to the paramagnetic force,  $F_{\text{mag2}}$  (Eqs. (10.83-10.84) and (10.89)). The positive root of Eq. (10.216) must be taken in order that  $r_n > 0$ . The radii of several  $n$ -electron atoms are given in Tables 10.3-10.8.

The ionization energy for the boron atom is given by Eq. (10.104). The ionization energies for the  $n$ -electron atoms are given by the negative of the electric energy,  $E(\text{electric})$ , (Eq. (10.102) with the radii,  $r_n$ , given by Eq. (10.216)):

$$E(\text{Ionization}) = -\text{Electric Energy} = \frac{(Z-(n-1))e^2}{8\pi\epsilon_0 r_n} \quad (10.217)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured  $n$ -electron atoms are given by Eqs. (10.217) and (10.216) in Tables 10.3-10.8.

Table 10.9. Summary of the parameters of five through ten-electron atoms.

Atom Type	Electron Configuration	Ground State Term <sup>a</sup>	Orbital Arrangement of 2p Electrons (2p state)	Diamagnetic Force Factor $A^b$	Paramagnetic Force Factor $B^c$
Neutral 5 e Atom <i>B</i>	$1s^2 2s^2 2p^1$	$^2P_{1/2}^0$	$\begin{array}{ccc} \uparrow & \text{---} & \text{---} \\ 1 & 0 & -1 \end{array}$	2	0
Neutral 6 e Atom <i>C</i>	$1s^2 2s^2 2p^2$	$^3P_0$	$\begin{array}{ccc} \uparrow & \uparrow & \text{---} \\ 1 & 0 & -1 \end{array}$	$\frac{2}{3}$	0
Neutral 7 e Atom <i>N</i>	$1s^2 2s^2 2p^3$	$^4S_{3/2}^0$	$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ 1 & 0 & -1 \end{array}$	$\frac{1}{3}$	1
Neutral 8 e Atom <i>O</i>	$1s^2 2s^2 2p^4$	$^3P_2$	$\begin{array}{ccc} \uparrow\downarrow & \uparrow & \uparrow \\ 1 & 0 & -1 \end{array}$	1	2
Neutral 9 e Atom <i>F</i>	$1s^2 2s^2 2p^5$	$^2P_{3/2}^0$	$\begin{array}{ccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ 1 & 0 & -1 \end{array}$	$\frac{2}{3}$	3
Neutral 10 e Atom <i>Ne</i>	$1s^2 2s^2 2p^6$	$^1S_0$	$\begin{array}{ccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ 1 & 0 & -1 \end{array}$	0	3
5 e Ion	$1s^2 2s^2 2p^1$	$^2P_{1/2}^0$	$\begin{array}{ccc} \uparrow & \text{---} & \text{---} \\ 1 & 0 & -1 \end{array}$	$\frac{5}{3}$	1
6 e Ion	$1s^2 2s^2 2p^2$	$^3P_0$	$\begin{array}{ccc} \uparrow & \uparrow & \text{---} \\ 1 & 0 & -1 \end{array}$	$\frac{5}{3}$	4
7 e Ion	$1s^2 2s^2 2p^3$	$^4S_{3/2}^0$	$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ 1 & 0 & -1 \end{array}$	$\frac{5}{3}$	6
8 e Ion	$1s^2 2s^2 2p^4$	$^3P_2$	$\begin{array}{ccc} \uparrow\downarrow & \uparrow & \uparrow \\ 1 & 0 & -1 \end{array}$	$\frac{5}{3}$	6
9 e Ion	$1s^2 2s^2 2p^5$	$^2P_{3/2}^0$	$\begin{array}{ccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ 1 & 0 & -1 \end{array}$	$\frac{5}{3}$	9
10 e Ion	$1s^2 2s^2 2p^6$	$^1S_0$	$\begin{array}{ccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ 1 & 0 & -1 \end{array}$	$\frac{5}{3}$	12

<sup>a</sup> The theoretical ground state terms match those given by NIST [8].<sup>b</sup> Eq. (10.82).<sup>c</sup> Eq. (10.83-10.84) and (10.89).

### References

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